Available online at www.sciencedirect.com

Journal of Photochemistry and Photobiology A: Chemistry 180 (2006) 282–288

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Control strategies for reactive processes involving vibrationally hot product states

Dorothee Geppert[*], Regina de Vivie-Riedle

LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

Received 5 January 2006; received in revised form 10 February 2006; accepted 13 February 2006
Available online 6 March 2006

Abstract

We present an all optical control mechanism for the switching process in fulgides via electronically excited states in the presence of conical intersections. The underlying photoreaction is the ring opening or closure of the central C_6-ring chromophore. The control of this reaction is realized with shaped laser pulses which are obtained by Optimal Control Theory. Our implementation of the algorithm enables the definition of a target in the electronic ground state even if vibrationally hot product states are formed during the reaction demanding the appliance of a damping function. We introduce a flexible target definition including all parts of the wavepacket that will reach the target region within a given time interval *T*. Thereby the localization of the wavepacket inside this region at a specific point in time is not mandatory. A target definition in the ground state facilitates the comparability to experiments. With this target, the control algorithm favors an all optical process which is faster than the relaxation through the conical intersections. To enhance the possibility of experimental realizations, we analyze the optimized pump–dump sequence to allow a reconstruction and simplification of the laser field.

Keywords: Optimal Control Theory; Molecular switches; Flexible target definition; Control of reactive processes

1. Introduction

Fulgides are considered as promising candidates for molecular switches [1–3] which can be used as active devices in nanotechnology and for the implementation of logic gates in molecular computation. They are bistable and their isomers can be distinguished by their physical properties. When used as the bridging unit between an electron donor and acceptor moiety they offer the possibility to alter the system's properties by a specific photochemical reaction. In the open form E (see Fig. 1), energy or electron transfer is possible, while the closed form C suppresses fluorescence but leads to a fast radiation–less decay [2]. In our present investigations, we concentrate on the switching process between these two isomers which is initialized by a laser excitation in the UV/vis. For an effective switch a very high quantum yield is necessary, thus we suggest to enhance the yield by the use of shaped femtosecond laser pulses. We use Optimal Control Theory (OCT) to find these optimal laser pulses. In an iterative scheme, the shape of the laser field which guides the wavepacket from the initial to the target state is optimized [4–8]. In the experiment, the optimized pulses are found in closed loop set-ups based on genetic algorithms and are constructed by phase and frequency modulation [9–13].

The control of reactive photochemical systems like fulgides exhibits several challenges. Parts of the reaction occur in an optically not accessible dark region. This requires the generation of an excited state wavepacket with well-defined features like shape and momentum which subsequently evolves on the hypersurface to the target in the ground state. In photoreactions like in fulgides, where an ultrafast return to the ground state via conical intersections is possible, vibrationally hot molecules are formed during the reaction. Their numerical treatment becomes challenging in the OCT algorithm where forward and backward propagations are needed.

From an experimental point of view, the excitation frequency lying in the ultraviolet is a solvable but demanding task for pulse shaping [14,15]. Therefore we analyze the theoretically optimized pulse to extract the parts essential for the switching process. Based on this knowledge, we try to approximate the optimal field by a sequence of simpler Gaussian laser pulses.

---

[*] Corresponding author. Tel.: +49 89 2180 77535; fax: +49 89 2180 77133.
E-mail addresses: Dorothee.Geppert@cup.uni-muenchen.de (D. Geppert), Regina.de_Vivie@cup.uni-muenchen.de (R. de Vivie-Riedle).

1010-6030/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.02.017

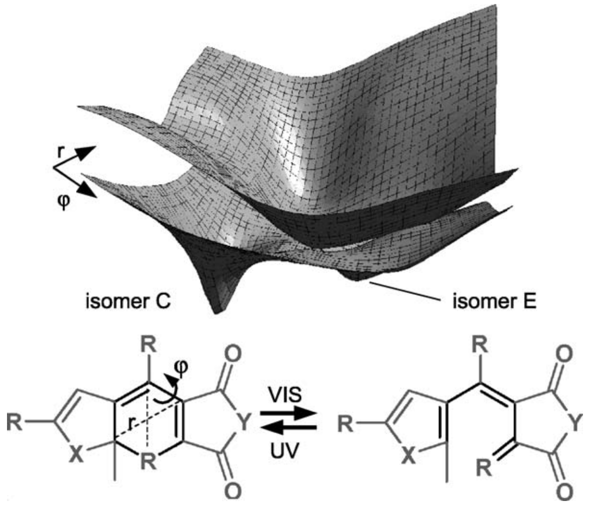

Fig. 1. The ring opening of a cyclohexadiene unit to an all-*cis* hexatriene unit constitutes the switching process of fulgides. The reactive coordinates *r* and *φ* are indicated. The two dimensional potential energy surfaces include both minima as well as two conical intersections connecting the excited state and the ground state.

2. The system under consideration

Fulgides exist in two stable isomers which can be swapped by a photochemical reaction (see Fig. 1). Their different absorption frequencies make them addressable individually and enable a selective read-out. The active center of these molecules consists of a cyclohexadiene/all-*cis* hexatriene subunit (indicated in black in Fig. 1). The opening or closure of this ring subunit is the decisive step in the switching process of the fulgides. Therefore we concentrate our investigations on the reaction of this subunit.

The ring opening of cyclohexadiene is a well known photochemical reaction following the Woodward–Hofmann rules that was studied experimentally [16–19] and theoretically [20–25]. After the excitation of cyclohexadiene the system evolves through various conical intersections leading to a branching into the ground states of both isomers cZc-hexatriene and cyclohexadiene which correspond to isomers E and C in fulgides, respectively. The following isomerizations of cZc-hexatriene to its more stable *trans*-isomers are not important for our considerations as they are sterically inhibited in fulgides. The most important features of this ring opening reaction can be described in two reactive coordinates r and φ (Fig. 1) introduced in [23]. The asymmetric squeezing of the ring is described by r and φ is the angle between the two indicated diagonals. There are two excited electronic states involved in the reaction. As it is known from experiments that the initially excited electronic state is depopulated completely within 10 fs [17], the coupling between these two states must be very strong. Therefore we treat the two crossing excited states as one adiabatic surface [25]. On the resulting potential energy surfaces, derived from interpolation between ab initio data points, we perform quantum dynamical calculations on a grid with the Chebychev propagation scheme [26,27]. The laser excitation is treated semi-classically and the effect of the conical intersections connecting the excited state with the ground state is calculated non-adiabatically with the coupling elements derived by quantum chemical calculations as described in [24]. In the following calculations, we regard the backward reaction, i.e. the ring closure from isomer E to isomer C.

3. Ground state target

The great challenge to control this reaction is made more difficult by the fact that parts of the excited state are not accessible by laser excitation. Only in the Franck–Condon regions of both isomers transition dipole moments of relevant size allow an optical transfer. Here a wavepacket must be prepared which subsequently propagates freely along the desired pathway. We could already demonstrate the control of this system within the framework of OCT in [25], where an intermediate target was used in the excited state. The intermediate target was a well-defined wavepacket with respect to magnitude and direction of momentum so that it evolved through a conical intersection to the desired target. This solution relies on a fast transfer through the conical intersections. However, this transfer is in general not completed in one step. Thus, the system has to reach the relevant conical intersection several times and a loss of control is inevitable if the conical intersections are located in an optically dark region as it is in this case. In addition, no direct experimental counterpart for the intermediate target is known so far. Therefore it is desirable to define the electronic ground state of the wanted isomer as the target state. If we try to do so, we encounter several challenges: after its return to the ground state through the conical intersections the wavepacket is vibrationally hot and its kinetic energy is high enough to reach the grid boundaries in the ground state. Due to the numerical implementation with periodic boundary conditions, the wavepacket must not evolve over the grid boundaries, but has to be damped away if it reaches them. In addition, we assume that the parts of the wavepacket which cross the minimum of isomer C will finally relax into this minimum. To mimic this process, the wavepacket is damped in the minimum of isomer C too, as there is no relaxation into other coordinates or a bath included in our system Hamiltonian. The real-valued damping function G, depicted in Fig. 2a), sets the corresponding parts of the wavefunction in the ground state to zero [28,29]. Thus, the damping function G is not connected to any dissipation process, but prevents the occurence of a non-physical reaction progress (e.g. switching to the other minimum in the ground state) by eliminating the affected parts of the wavepacket from the subsequent dynamical calculation. This damping process complicates the backward propagation needed in the optimal control algorithm. In OCT, the optimal laser field is found by simultaneous propagations of the initial wavefunction Ψ and the target wavefunction λ. Backward propagation becomes necessary because initial and final state are defined at different points in time, namely at $t = 0$ and $t = T$ which is the maximum duration time of the laser field. When a spatial projection operator P is used to define the target region, the target wavefunction λ is built by letting P act on Ψ.