Coherent control for ultrafast photochemical reactions*

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Abstract: Many photochemical processes involving the breaking and formation of chemical bonds take place on a femtosecond time scale. By means of ultrafast laser pulses it became possible to monitor these events in real time with a temporal resolution in the sub-20 fs regime. Moving beyond the observation to the control of chemical reactions requires additional theoretical and experimental effort. We illustrate with the aid of selected model systems the concepts and possibilities of "passive" and "active" control and their differences.

INTRODUCTION

The field of coherent control has been stimulated by the objectives of selective bond breaking and formation. First concepts for controlling chemical reactions in the time domain with ultrashort laser pulses have been developed theoretically by Tannor, Rice, and Kosloff [1] and realized experimentally by Gerber [2] and Zewail [3]. In this pump-dump approach the system can be influenced by varying the pump pulse parameters and the delay time between pump and probe pulse. An extension of this concept to self-learning control was outlined by Rabitz and coworkers [4–6]. The basic principle relies on closed-loop learning algorithms to optimize the laser fields and leads to the concepts of optimal control theory (OCT). The shape of the laser field is optimized to guide the chemical reaction from the initial to the final state.

With two examples both concepts will be illustrated. The principle of initial state preparation by variation of the pump pulse parameters is discussed for the photochemical ring opening of cyclohexadiene ("passive" control) [7]. This reaction is mediated by at least two conical intersections allowing for the ultrafast, barrierless transition to the ground state. The aim is to drive the reaction systematically toward the two conical intersections to influence the resulting product distribution. OCT strategies ("active" control) are discussed for a bimolecular reaction also guided by a conical intersection. The model system is Na*H_2 with the objective to manipulate the quenching process [8].

MODEL AND THEORY

In photoinduced chemical processes often several potential surfaces are involved. In the language of quantum mechanics the interaction between molecule and light is described in form of the time-dependent Schrödinger equation. For two potential energy surfaces V_g and V_e coupled in semiclassical dipole approximation, the Schrödinger equation reads as:

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = \left\{ \begin{pmatrix} T + V_g & V_{ge} \\ V_{eg} & T + V_e \end{pmatrix} - \varepsilon(t) \begin{pmatrix} 0 & \mu_{ge} \\ \mu_{eg} & 0 \end{pmatrix} \right\} \Psi(t)$$

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where V_{eg} is a possible time-independent coupling and μ_{eg} the transition dipole moment. Fourier limited femtosecond pulses are usually approximated by a Gaussian or sech function.

In principle, the laser field $\varepsilon(t)$ can be varied in frequency, phase, and amplitude. The prepared wavepacket is a coherent superposition of vibrational eigenstates:

$$|\Psi(t)\rangle = c_1|\chi_1\rangle e^{i\omega_1 t} + c_2|\chi_2\rangle e^{i\omega_2 t} + ...$$

$$|\Psi(t)|^2 = |c_1\chi_1|^2 + |c_2\chi_2|^2 + c_1^* c_2 \cos[(\omega_1 - \omega_2)t]\chi_1^*\chi_2 + ...$$

The coherence is reflected in the cosine dependent interference term of the density function. In our context the term "passive" control is used, when particular wavepackets are prepared in the Franck–Condon (FC) region by different pump laser pulses which are then turned off. In this case, the weight of the partial waves does not change after pump pulse excitation, the change of the density is only due to the time-dependent phases such that the wavepackets evolve only under the influence of the potential surfaces (see Fig. 1, dashed line). The term "active" control is used when the laser field remains turned on until the intended reaction is finished (Fig. 1, solid line). In this case, the laser field guides the system from the initial state out of the FC region to the final outcome, which means that the coefficients c_i stay time dependent during the whole reaction, allowing for a more direct influence of the laser light.
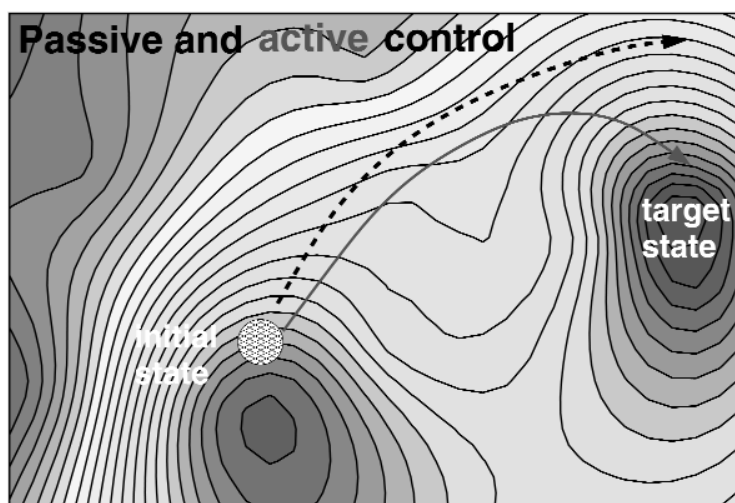
Fig. 1 Schematic representation of passive (dashed line) and active control of a reaction from the initial state to the target state.

To find the optimal laser field for different objectives means to tune simultaneously the multiple parameters provided by an ultrashort laser pulse. This can be achieved either by hand optimization or by applying fast convergent optimal control algorithms. These algorithms can be applied to manipulate population transfer from a definite initial to a specific final state as well as to maximize expectation values, i.e., to prepare a particularly shaped wavepacket at a selected area on the reaction surface.

For the analytical determination of the optimal laser field which drives the system from an initial state $\Psi_i(0)$ at $t = 0$ to the selected target area $X\Psi_i(T)$ at time $t = T$, with X the actual space operator, the subsequent functional has to be evaluated:

$$L[\Psi_i(t), \Psi_f(t), \varepsilon(t)] = \left| \langle \Psi_i(T) \mid X \mid \Psi_i(T) \rangle \right|^2 - \alpha_0 \int_0^T \frac{|\varepsilon(t)|^2}{s(t)} \, dt$$

$$- 4 \, \mathrm{Re} \left\{ \langle \Psi_i(T) | X | \Psi_i(T) \rangle \cdot \int_0^T \langle \Psi_f(t) | \frac{i}{\hbar} [H - \mu\varepsilon(t)] + \frac{\partial}{\partial t} | \Psi_i(t) \rangle dt \right\}.$$

The field optimization is reduced to find the maximum of the functional *L* which is solved by the variation of its three variables and leads to the subsequent set of coupled differential equations:

$$\varepsilon(t) = - \frac{s(t)}{\hbar\alpha_0} \cdot \mathrm{Im} \left\{ \langle \Psi_i(T) | X | \Psi_i(T) \rangle \langle \Psi_f(t) | \mu | \Psi_i(t) \rangle \right\} \quad ,$$

$$i\hbar \frac{\partial}{\partial t} \Psi_i(t) = [H - \mu\varepsilon(t)] \Psi_i(t) \ \ with \ \ \Psi_i(0) = \Phi_i \quad \quad ,$$

$$i\hbar \frac{\partial}{\partial t} \Psi_f(t) = [H - \mu\varepsilon(t)] \Psi_f(t) \ \ with \ \ \Psi_f(T) = X\Psi_i(T) \quad .$$

The first equation represents the optimal electric field in terms of the evolving wavepackets Ψ_i and Ψ_f and the next two guarantee their compliance with the Schrödinger equation under the influence of the laser field $\varepsilon(t)$. To satisfy the demand of smooth switch on and off behavior of the laserfield the shape function $s(t)$ is introduced. The parameter α_0 limits the time averaged laser intensity and T denotes the overall pulse duration.

This set of nonlinear differential equations is computed iteratively with each iteration producing a new field ε_{new} increasing the value of the functional *L*.

PASSIVE AND ACTIVE CONTROL

With the aid of selected model systems the concepts and possibilities of passive and active control and their differences are illustrated.

The principle of initial state preparation (passive control) is applied to the photoinduced ring opening of cylcohexadiene. This reaction is facilitated by conical intersections [9,10]. In the S_1/S_0 transition at least two conical intersections that differ in their energetic and spatial location are involved [7]. Both conical intersections will induce a branching on the ground-state surface leading to different products, vibrational excited cyclohexadiene and hexatriene. However, the resulting product distribution differs for the two conical intersections. The energetically lower conical intersection leads to a roughly 50:50 distribution, while the higher lying conical intersection leads to an enhanced yield of hexatriene. The wavepacket prepared by the pump laser evolves on the excited S_1 state and starts to bifurcate within a few femtoseconds. Due to this quantum effect both conical intersections can be reached. The bifurcation is strongly influenced by the initial preparation achieved by variation of the pump pulse parameters, thereby allowing the passive control of the product yield.

To gain more, in our sense active, control on a molecular system, we employ OCT to localize a wavepacket at a selected conical intersection. As model system we chose the exciplex Na*H_2 [8], formed by excitation during the collision of Na + H_2(v = 0). The complex also provides a reachable conical intersection which can be regarded as a kind of reaction center where electronic energy is transferred into vibrational energy. On the way through the conical intersection the system changes from the bonding type to the antibonding distribution repelling the now vibrationally excited H_2 fragment.

Control of expectation values is performed to localize a wavepacket at the lowest lying conical intersection of the collision exciplex Na*H_2. It was possible to prepare a highly localized wavepacket close to the conical intersection and follow afterwards the quenching process on a microscopic scale, revealing that only the wavepacket motion along the Na–H_2 guides the reaction. The velocity of the

relaxation process from the excited surface to the ground state through the conical intersection could be influenced by the form of the wavepacket prepared at the conical intersection. The final influence on the vibrational distribution of the H_2 fragment is project to further investigations.

CONCLUSION

Ultrafast laser pulses provide a flexible and powerful tool not only to observe but also to control chemical and physical processes. Already by initial state preparation, i.e., passive control, the molecular system can be manipulated in sophisticated ways and final product yields can be controlled. The degree of control can be enhanced by active control with the help of OCT concepts. We could show for the model system NaH_2 that it is possible to selectively focus a shaped wavepacket at a conical intersection and that this possibility has indeed an effect on the outcome of the subsequent reaction. In the future we will apply the same concept of active control to drive the cyclohexadiene-hexatriene system selectively through one of its conical intersections, and thereby control directly the distribution of product states.

The selected examples demonstrate that ultrafast laser pulses provide a flexible and powerful tool not only to observe but also to control photochemical processes. Already by initial state preparation, i.e., passive control, the molecular system can be manipulated in a defined way. The degree of control can be enhanced by active control with the help of OCT concepts.

REFERENCES

1. D. J. Tannor and S. A. Rice. *J. Chem. Phys.* **83**, 5013 (1985); D. J. Tannor, R. Kosloff, S. A. Rice. *J. Chem. Phys.* **85**, 5805 (1986).
2. T. Baumert and G. Gerber. *Isr. J. Chem.* **34**, 103 (1985).
3. A. H. Zewail. *Adv. Chem. Phys.* **101**, 3 (1997).
4. W. Zhu, J. Botina, H. Rabitz. *J. Chem. Phys.* **108**, 1953 (1998).
5. W. Zhu and H. Rabitz. *J. Chem. Phys.* **111**, 472 (1999).
6. H. Rabitz, R. de Vivie-Riedle, M. Motzkus, K. Kompa. *Science* **288**, 824 (2000).
7. A. Hofmann and R. de Vivie-Riedle. *J. Chem. Phys.* **112**, 5054 (2000).
8. R. de Vivie-Riedle, K. Sundermann, M. Motzkus. *Faraday Discuss.* **113**, 303 (1999).
9. S. Lochbrunner, W. Fuß, W. E. Schmid, K. L. Kompa. *J. Phys. Chem. A* **102**, 9334 (1998).
10. S. H. Pullen, N. A. Anderson, L. A. Walker, II, R. J. Sension. *J. Chem. Phys.* **108**, 556 (1998).