SYQS 1: Quantum Control Spectroscopy I

Time: Thursday 10:30–12:30 Location: E 415

Invited Talk SYQS 1.1 Th 10:30 E 415

Theoretical studies on quantum control and spectroscopy of ultrafast photoreactions — •Regina de Vivie-Riedle[1], Judith Voll[1], Artur Nenov[1], Tiago Buckup[2], Jürgen Hauer[2], and Marcus Motzkus[2] — [1]LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany — [2]Physikalische Chemie, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg

We are interested in the spectroscopy and control of ultrafast photoreactions, key elements in chemical and biological processes. We approach this topic from the quantum chemical and quantum dynamical side. Often a seam of conical intersections provides the locus for the ultrafast transfer between electronic states and thus the topography experienced by the ongoing reaction. Features decisive for a photoreaction will be illustrated by a calculated complete seam. Possible reaction pathways are classified as well as routes for optical control. Pulse sequences as optimal light fields often emerged in experimental as well as in theoretical studies. Their excitation mechanism is explored using the example of an open quantum system set up in the density formalism and adapted to the experimentally investigated beta carotene [1]. We discuss and explain the effect of the individual pulse parameters [2], relate them to the system response and outline a strategy for the use of pulse trains in spectroscopy and signal processing.

[1] J. Hauer et al.,Chem. Phys. Lett., 421, (2006) 523.
[2] J. Voll et al., New J. Phys., 11 (2009), 105036.

Invited Talk SYQS 1.2 Th 11:00 E 415

Quantum Control Spectroscopy: Understanding photobiology with coherently controlled matter waves — •Tiago Buckup[1,2], Jürgen Hauer[3], Judith Voll[4], Regina Vivie-Riedle[4], and Marcus Motzkus[1,2] — [1]Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität, D-69120 Heidelberg, Germany. — [2]Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany. — [3]Department of Physical Chemistry, University of Vienna, A-1090 Vienna, Austria. — [4]Department Chemie, Ludwig-Maximilians-Universität, D-81377 München, Germany.

The combination of coherent control methods with time-resolved spectroscopy, namely Quantum Control Spectroscopy (QCS), is a compelling approach to disentangle ultrafast dynamics [1]. In particular, QCS can be very rewarding to investigate complex systems, such as light-harvesting complexes, where very often the traditional pump-probe spectroscopy fails. We report an experiment using phase-modulated degenerate four-wave mixing and provide a general mechanism for phase-only control of an open quantum system with an ultrashort excited state lifetime. We show by the use of coherent control that a low-frequency bending motion (178 cm^{-1} in β-carotene) is the driving force behind the photophysically relevant step in carotenoids, a central constituent of many light harvesting complexes. We can now rationalize pulse shapes found in a whole class of quantum control experiments, ranging from simple dye molecules to embed-protein chromophores like all-trans-retinal in bacteriorhodopsin.

[1] Wohlleben, W. et al., ChemPhysChem 6 (2005) 850.

Invited Talk SYQS 1.3 Th 11:30 E 415

Development of strategies for the optimal control in complex systems — •Roland Mitric — Fachbereich Physik, Arnimallee 14, D-14195 Berlin

A newly developed *Field induced surface hopping* method for simulation and control of laser induced processes in complex molecular systems will be presented. This method combines quantum electronic state population dynamics with classical nuclear dynamics carried out *on the fly* and can be connected with optimal control in order to steer molecular processes by optimizing laser fields using e. g. evolutionary algorithms. For the propagation of classical trajectories the whole spectrum of methods ranging from empirical force fields, semiempirical to ab initio quantum chemical methods can be employed, opening the possibility of broad applications. Furthermore our approach allows to gain a fundamental insight into the mechanisms underlying the control of molecular processes by direct application of experimentally optimized laser pulses. We will illustrate our approach on the examples of the control of photoswitching (trans-cis isomerization), control of excited state lifetimes and photoemission in DNA bases and optical discrimination of flavine chromophores. References: R. Mitric, J. Petersen, V. Bonacic-Koutecky, Phys. Rev. A., 79, 053416 (2009)

Invited Talk SYQS 1.4 Th 12:00 E 415

Mechanistic laser pulse parameterizations — •Tobias Brixner — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Shaped femtosecond laser pulses offer a powerful tool for coherent control. Depending on the type of problem, the optimal parameterization of phase, amplitude, and polarization properties may differ, especially if mechanistic insight is desired in addition to control performance. Here, several types of parameterization for femtosecond laser pulses will be discussed.

In the first case, control of the so-called Wolff rearrangement offers an example for a photochemical bond-breaking and bond-formation reaction in liquid phase, and non-restricted adaptive pulse shaping is compared with linear-chirp and spectral triangular-phase parameterizations. In the second example, the von Neumann time-frequency distribution is introduced and applications in molecular control are suggested. Experimental quantum control landscapes are recorded, and the performance in adaptive optimizations is compared with the pulse-shaper pixel basis. In the third example, the parameterization is chosen such that the control mechanisms in ultrafast nano-optics are mirrored exactly. Thus a generally valid analytic solution for the control problem is found, and the global optimum is obtained in a direct, non-iterative fashion. First experiments using the analytic solution confirm these predictions.