

MO 2: Quantum Control

Time: Monday 11:30–13:00

Location: PH/HS1

Invited Talk

MO 2.1 Mon 11:30 PH/HS1
Simulating the control of molecular reactions via modulated light fields: From gas phase to solution — ●REGINA DE VIVIE-RIEDLE — LMU München

Optimal control theory and optimal control experiments are state-of-the-art tools to control quantum systems. Both methods have been demonstrated successfully for numerous applications in molecular physics, chemistry and biology. Modulated light pulses could be realized, driving these various control processes. The accessibility of few femtosecond or even attosecond pulses opens the door further to direct observation and steering of electron dynamics. Next to the control efficiency, a key issue is the understanding of the control mechanism. An obvious way is to seek support from theory. In this contribution theoretical studies will be presented that highlight control events ranging from chemical reactions via the steering of nuclear and electronic wavepackets [1,2,3] over directional control of bond breaking in symmetric molecules [4] to control scenarios in solution.

[1] P. von den Hoff, S. Thallmair, M. Kowalewski, R. Siemering, and R. de Vivie-Riedle, *Phys. Chem. Chem. Phys.* 14 (2012), 14460-14485.

[2] M. Kling, P. von den Hoff, I. Znakovskaya, and R. de Vivie-Riedle, *Phys. Chem. Chem. Phys.* 15 (2013), 9448-9467.

[3] S. Thallmair, R. Siemering, P. Kölle, M. Kling, M. Wollenhaupt, T. Baumert, and R. de Vivie-Riedle, in: *Molecular quantum dynamics - from theory to applications*, F. Gatti (Ed.), Springer, 2014, 213-248.

[4] A. S. Alnaser, et al. *Nat. Commun.* 5, article number: 3800 (2014).

MO 2.2 Mon 12:00 PH/HS1

Combination of Chirped and Multipulse Excitation: Control of Population and Vibrational Coherence — ●ELISABETH BRÜHL¹, IDUABO JOHN AFA², CARLES SERRAT², TIAGO BUCKUP¹, and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Universitat Politècnica de Catalunya, Department de Física i Enginyeria Nuclear, Colom 11, 08222 Terrassa, Spain

Tailoring molecular vibrations is a potential control knob to steer photochemical reactions. Electronic near-resonant excitation with multipulses has been shown to enhance vibrational coherence in the excited state [1]. Additionally, vibrational coherence of the ground state can be also manipulated by using chirped pump pulses via intrapulse impulsive Raman scattering [2]. These two methods of mode selective control with tailored pump beams are now combined to tailor vibrational coherence and population in the electronic excited as well as in the ground state. This is demonstrated by systematic phase shaping of the excitation pulse in transient absorption of dye molecules. A four-level density matrix model is developed to simulate the enhancement and suppression of population and vibrational coherence using such chirped multipulse excitation. The effect of overlap between the excitation and absorption spectra, the degree of chirped excitation and the role of the molecular mode frequency are discussed.

[1] Buckup et al., *JPB* 2008, 41, 074024.

[2] Wand et al., *PCCP* 2010, 12, 2149.

MO 2.3 Mon 12:15 PH/HS1

Photoassociation of hot magnesium atoms by phase-shaped femtosecond pulses — ●WOJCIECH SKOMOROWSKI¹, LIAT LEVIN², LEONID RYBAK², RONNIE KOSLOFF³, CHRISTIANE P. KOCH¹, and ZOHAR AMITAY² — ¹Theoretische Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany — ²The Shirlee Jacobs Femtosecond Laser Research Laboratory, Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel — ³Fritz Haber Research Centre and The Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel

One of the long-standing goals in the field of coherent control is the

control of photo-induced bimolecular chemical reactions. Realizing this goal will create a new type of photochemistry with selective control of yields and branching ratios. Shaped laser pulses can act there as special catalysts which drive molecular process to a desired channel. Here we show coherent control of bond making, a milestone on the way to the control of photo-induced chemical reactions. The control is demonstrated in the process of multiphoton photoassociation of hot magnesium atoms by phase-shaped femtosecond laser pulses. We find the yield of observed Mg₂ molecules to be strongly enhanced for positively chirped pulses and suppressed for negatively chirped pulses. Our fully *ab initio* model, combining electronic structure calculations with quantum molecular dynamics, shows that control is achieved by purification via Franck-Condon filtering coupled with chirp-dependent Raman transitions. The presented results prove that coherent control of binary photo-reactions is feasible even under thermal conditions.

MO 2.4 Mon 12:30 PH/HS1

Quantum optimal control of a carbonyl reaction in an explicit solvent cage using tailored laser pulses — ●DANIEL KEEFER, SEBASTIAN THALLMAIR, and REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

Influencing the outcome of a chemical reaction is an everyday struggle for chemists. A powerful tool to directly interact with a molecular process is to address its quantum nature, which is achieved by using specifically tailored laser pulses. Theoretically, the tailoring is accomplished using optimal control theory (OCT).

Investigating a chemical process which takes place in solution, a proper theoretical treatment becomes more challenging. Electrostatic and dynamic solvent effects influence the quantum dynamical behaviour during the ultrafast reaction. We present a way to account for these effects in OCT optimizations. Therefore, a QD/MD approach combining quantum dynamics (QD) and classical molecular dynamics (MD) is used. The motion of the explicitly included solvent molecules around the reactant is described by MD. Different solvent cage arrangements are extracted from the MD trajectories. These arrangements alter the potential energy surface for the chemical reaction in different ways. The various solvent cage configurations are included in the Hamiltonian to approximate the thermodynamical distribution of the solvent molecules in the solution. Optimizations are conducted to obtain laser pulses for optimal control of an ensemble of solvent arrangements. Significant effects on the shape of the laser pulses controlling the reaction are observed.

MO 2.5 Mon 12:45 PH/HS1

Phase-controlled polarization decay and line-shape modifications in complex systems — ●KRISTINA MEYER, ZUOYE LIU, NIKLAS MÜLLER, and THOMAS PFEIFER — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

Recently, our group demonstrated the transformation of Fano to Lorentzian line shapes and vice versa in time-resolved absorption experiments in helium. This was realized by inducing phase changes in the singly and doubly excited states by means of laser pulses, enabling the control of the optical dipole response [1]. Now, we show that this mechanism can be generalized to more complex systems in the liquid phase. For this purpose, we performed transient-absorption measurements in the dye molecule IR144 dissolved in methanol. By applying 7-fs short NIR laser pulses significant modifications of the IR144 absorption spectrum could be observed. In order to investigate if the measured line-shape changes could originate from the same Fano-phase formalism as derived for the case of helium, we carried out a numerical simulation. The extremely good qualitative agreement of simulation and experiment proves the universal applicability of the phase-control mechanism to complex systems.

[1] C. Ott et al., *Science* 340, 716 (2013)