

## MO 14: Ultrafast Multidimensional and Control Approaches

Time: Wednesday 14:00–16:00

Location: S HS 001 Biologie

MO 14.1 Wed 14:00 S HS 001 Biologie

**Probing Phosphate-Magnesium Ion Interactions in Water using Ultrafast 2D-IR spectroscopy** — ●JAKOB SCHAUSS, FABIAN DAHMS, BENJAMIN P. FINGERHUT, and THOMAS ELSAESSER — Max Born Institute for Nonlinear Optics and Short-Pulse Spectroscopy, Berlin, Germany

Biomolecules are fundamentally affected by electric interactions with their surrounding solvent shell and the embedded ions.  $Mg^{2+}$ -ions are known to play a vital role in stabilizing RNA geometries, yet the underlying interactions are mainly unresolved. To unravel microscopic couplings and dynamics, non-invasive molecular probes are required, such as the phosphate vibrations of the nucleic acid backbone.

We used femtosecond 2D-IR spectroscopy on the dimethylphosphate anion  $DMP^-$ , an established model system of the DNA/RNA backbone, and were able to observe a distinct blue shift of the asymmetric stretch vibration  $\nu_{as}(PO_2)^-$  when magnesium ions were added. Concomitant theoretical ab-initio simulations attribute this frequency shift to the formation of contact  $DMP^-/Mg^{2+}$  ion pairs, providing a handle to distinguish site-bound and diffuse ions in biomolecular systems in future research.

MO 14.2 Wed 14:15 S HS 001 Biologie

**Rapid coherent three-dimensional fluorescence spectroscopy disentangles quantum pathways of a molecular dianion** — ●STEFAN MÜLLER<sup>1</sup>, JULIAN LÜTTIG<sup>1</sup>, LEI JI<sup>2</sup>, JIE HAN<sup>3</sup>, MICHAEL MOOS<sup>5</sup>, TODD B. MARDER<sup>2</sup>, UWE H. F. BUNZ<sup>4</sup>, ANDREAS DREUW<sup>3</sup>, CHRISTOPH LAMBERT<sup>5</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>3</sup>Physikalisches-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 205, 69120 Heidelberg — <sup>4</sup>Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg — <sup>5</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We developed a rapid shot-to-shot operating single-beam setup for electronic three-dimensional (3D) spectroscopy that uses fluorescence as an observable [1]. With this, we systematically acquire various types of 3D spectra, including multiple-quantum coherences, simultaneously, background free, inherently phased and within a few minutes. This allows us to study systems of limited chemical stability, such as the dianion of TIPS-tetraazapentacene [2]. Using a 125-fold phase cycling scheme, we isolate multiple 3D spectra that provide rich information up to sixth order in perturbation theory, revealing electronic coupling, nuclear wavepacket dynamics, highly-excited states, and more.

[1] S. Draeger et al., *Opt. Express* **25**, 3259 (2017).[2] L. Ji et al., *J. Am. Chem. Soc.* **139**, 15968-15976 (2017).

MO 14.3 Wed 14:30 S HS 001 Biologie

**Signatures of dipole-dipole interaction in 2D-spectroscopic signals of atomic gases** — ●BENEDIKT AMES, EDOARDO CARNIO, VYACHESLAV SHATOKHIN, and ANDREAS BUCHLEITNER — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Recent experimental studies have revealed collective effects in 2D fluorescence spectra of dilute atomic gases. These signals persist down to the lowest experimentally accessible densities on the order of  $10^7 \text{ cm}^{-3}$  [1]. Given the large interatomic distances in this regime, the exchange of transverse photons is expected to play a significant role in the dipole-dipole interaction.

In order to identify the dominant contributions to the latter, we investigate a model that includes the retarded interaction as mediated by the quantized field and as such is valid across all length scales. In a first approach, we study the time evolution of the system in a master equation formulation that has previously been applied to coherent backscattering in the double scattering regime [2]. Secondly, we treat the same system perturbatively in the atom-laser coupling. By varying the strength of the coupling, we establish conditions under which the master equation approach yields the same results as the perturbative calculation.

[1] L. Bruder, M. Binz, F. Stienkemeier, *Phys. Rev. A* **92**, 053412 (2015)[2] V. Shatokhin, C. Müller, A. Buchleitner, *Phys. Rev. A* **73**, 063813

(2006)

MO 14.4 Wed 14:45 S HS 001 Biologie

**Theoretical treatment of many-body signals in nonlinear phase-modulated spectroscopy** — ●GHASSAN ABUMWIS and ALEXANDER EISFELD — MIPPKS, Dresden, Germany

Using nonlinear phase-modulated spectroscopy, strong many-body signals have been observed in very dilute atomic gases [1,2]. So far, a theoretical explanation of these unexpected strong signals is missing. By extending the theoretical treatment of [3] we provide a possible explanation of the measurements.

[1]Bruder et al, *Phys. Rev. A* **92**, 053412 (2015)[2]Bruder et al, *Phys Chem Chem Phys*,(2018)DOI:10.1039/c8cp05851b[3]Li et al, *Phys. Rev. A* **95**, 052509 (2017)

MO 14.5 Wed 15:00 S HS 001 Biologie

**Excited state Rabi-cycling near the ionization threshold after multiphoton excitation - a general concept?** — ●TOM RING, HENDRIKE BRAUN, ALEXANDER KASTNER, CONSTANTIN WITTE, HAN-GYEOL LEE, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, 34132 Kassel, Germany

Control schemes using ultrashort laser pulses in the weak field regime such as the basic  $I^n$  behaviour and spectral interference as well as in the strong field regime such as Rabi-cycling, rapid adiabatic passage, photon locking or selective population of dressed states are well established. The excitation of molecules and atoms with near infrared femtosecond laser pulses can merge these regimes: In many cases the first excitation step is predominantly non-resonant (weak field interaction) while the increasing density of states near the ionization threshold results in the possibility of subsequent one-photon absorptions which can lead to excited state Rabi-cycling (strong field interaction).

To investigate coherent dynamics of atoms and molecules in this combination region we employ 2d strong field spectroscopy using sequences of phase modulated femtosecond laser pulses. Varying the relative optical phase and the temporal separation between adjacent pulses allows to look at the coherent response of the atomic level as well as molecular systems in the form of electronic coherences. Comparison of our experimental results with simulations confirms the subsequent weak and strong field behaviour.

MO 14.6 Wed 15:15 S HS 001 Biologie

**Coherent control of two-photon absorption via entangled photons** — ●EDOARDO CARNIO<sup>1</sup>, FRANK SCHLAWIN<sup>2</sup>, and ANDREAS BUCHLEITNER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Albert-Ludwigs Universität Freiburg, Germany — <sup>2</sup>Clarendon Laboratory, University of Oxford, United Kingdom

Coherent control exploits the coherence of classical light to drive an initial quantum state to a desired final state. In two-photon absorption (TPA), in particular, two photons are used to excite a molecule from the ground to an excited state. Under certain conditions, frequency-entangled photons drive the transition more efficiently than in the classical case [1]. We first show how this enhancement correlates with the entropy of entanglement of the two-photon state, both in the transient and in the steady states. We then extend our analysis to the case of a manifold of intermediate states, where we aim to control specific excitation pathways with the appropriate design of the two-photon states.

[1] Schlawin, F. & Buchleitner, A. *Theory of coherent control with quantum light*. *New J. Phys.* **19**, 013009 (2017).

MO 14.7 Wed 15:30 S HS 001 Biologie

**Phase control of complex Fano resonances** — ●NICOLA MAYER, MISHA IVANOV, and OLEG KORNILOV — Max Born Institute, Max-Born-Straße 2A, 12489 Berlin, Germany.

Complex Fano resonances are quantum mechanical systems consisting of two or more discrete states coupled to one or more common continua. If the coupling strength to the continuum is comparable to the energy separation between discrete states, an increase of coupling strength leads to a counterintuitive increase of lifetime of one of the discrete states, while the lifetime of the other becomes shorter. This phenomenon is known as interference stabilization [1]. In a previous

publication, we showed that this effect may occur in a complex autoionizing resonance in molecular nitrogen [2]. In this contribution, we explore the possibility of controlling the autoionization and population dynamics by using an auxiliary laser pulse. We develop a model for photoelectron experiments employing a three pulse scheme: an XUV pulse is used to excite the autoionizing states, a concomitant control NIR/VIS/UV pulse induces a relative phase shift between the autoionizing amplitudes and the resulting population dynamics is probed by a delayed NIR pulse. We show that depending on the relative phase induced by the control pulse, it is possible to selectively excite the long- or short-lived autoionizing states. Our results pave the way for future experiments where the control pulse sequences can be used both to steer the autoionization dynamics in the well-studied systems and applied as a spectroscopic tool to retrieve the intrinsic electron configuration interaction in unexplored systems.

MO 14.8 Wed 15:45 S HS 001 Biologie  
**Quantum Control with Quantum Light of Non-Adiabaticity in Molecules** — ANDRÁS CSEHI<sup>1</sup>, GÁBOR J. HALÁSZ<sup>1</sup>, ÁGNES

VIBÓK<sup>1</sup> und MARKUS KOWALEWSKI<sup>2</sup> — <sup>1</sup>Department of Theoretical Physics, University of Debrecen, H-40410 Debrecen, PO Box 5, Hungary — <sup>2</sup>Department of Physics, AlbaNova University Center, Stockholm University, 10691 Stockholm, Sweden

Coherent control in molecules is usually done with laser fields. The electric field is described classically and control over the time evolution of the system is achieved by shaping the phase and amplitude of laser pulses in the time or frequency domain. Moving on from a classical description to a quantum description of the light field enables us to engineer the quantum state of light and allows to manipulate the light-matter interaction in phase space instead. In this paper we will demonstrate the different principles of control with quantum light on the avoided crossing in lithium fluoride. Using a quantum description of light together with the non-adiabatic couplings and vibronic degrees of freedom opens up new ways to look at quantum control. We will show the deviations from control with purely classical light field and how back action of the light field becomes important in a few photon regime.