

MO 9: Femtosecond Spectroscopy II

Time: Wednesday 10:30–12:00

Location: MO-H5

MO 9.1 Wed 10:30 MO-H5

Direct Comparison of Molecular-Beam versus Liquid-Phase Pump-Probe and Two-Dimensional Spectroscopy on the Example of Azulene — ●HANS-PETER SOLOWAN¹, PAVEL MALÝ^{1,2}, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Faculty of Mathematics and Physics, Charles University, Prague, Ke Karlovu 5, 121 16 Praha 2, Czech Republic

With mass-resolved ion detection, we have introduced cations as a new observable in coherent two-dimensional (2D) spectroscopy [1]. Here we present new results of molecular-beam coherent 2D electronic spectroscopy on the example of azulene. We directly compare these gas-phase with liquid-phase measurements of azulene dissolved in cyclohexane. Both schemes probe the same Liouville-space pathway from S_0 to S_2 . Furthermore we show the S_1 excitation dynamics of azulene obtained by pump-probe measurements in both phases and discuss results with respect to a passage through a conical intersection between azulene's S_1 and S_0 state. The comparison allows us to isolate the influence of the environment of the molecule on its excited-state dynamics.

[1] S. Roeding and T. Brixner, *Nat. Commun.* **9**, 2519 (2018)

MO 9.2 Wed 10:45 MO-H5

Generation and compression of 10-fs deep ultraviolet pulses at high repetition rate using standard optics — ●LUKAS BRUDER¹, LUKAS WITTENBECHER^{2,3,5}, PAVEL KOLESNICHENKO^{3,4,5}, and DONATAS ZIGMANTAS^{3,5} — ¹Institute of Physics, University of Freiburg, Germany — ²Department of Physics, Lund University, 221 00 Lund, Sweden — ³NanoLund, Lund University, 221 00 Lund, Sweden — ⁴Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ⁵Chemical Physics, Lund University, 221 00 Lund, Sweden

The generation of deep ultraviolet optical pulses featuring broad spectral bandwidth and short pulse durations is a challenging task, especially when using high repetition rate (> 100 kHz) laser systems that provide only low pulse energies (< 10 μ J). Based on achromatic phase matching [1], we have accomplished the efficient generation of sub-10-fs pulses at a repetition rate of 200 kHz, tunable in the wavelength range 250–320 nm [2]. We also simplified the pulse compression scheme, avoiding adaptive optics.

[1] P. Baum et al., *Opt. Lett.* **29**, 1686 (2004)

[2] L. Bruder et al., *Opt. Express* **29**, 25593 (2021)

MO 9.3 Wed 11:00 MO-H5

Tracking Ultrafast Exciton-Exciton Annihilation in a Squaraine Dimer by Sixth-Order Fluorescence-Detected Two-Dimensional Spectroscopy — ●STEFAN MÜLLER¹, PAVEL MALÝ¹, JULIAN LÜTTIG¹, CHRISTOPH LAMBERT², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Exciton-exciton annihilation (EEA), that is, the loss of one exciton through the interaction with another exciton, is an integral part of the excitation dynamics in molecular aggregates under high light irradiation. Through recent developments, the dynamics of EEA can be measured directly by coherently detected fifth-order two-dimensional (2D) spectroscopy, whereby the properties of exciton diffusion can also be determined [1]. Nonetheless, it is challenging to isolate ultrafast annihilation events as they may be obscured by coherent artifacts and nonresonant response. Here we introduce a novel 2D spectroscopic method to temporally resolve ultrafast EEA by detecting fluorescence and using only a single excitation beam. This is achieved by isolating specific sixth-order signals via 125-fold phase cycling of a collinear four-pulse excitation sequence [2]. We verify our approach on a squaraine heterodimer with aid of fifth-order 2D spectroscopy [3].

[1] J. Dostál et al., *Nat. Commun.* **9**, 2466 (2018).

[2] S. Mueller et al., *Nat. Commun.* **10**, 4735 (2019).

[3] P. Malý et al., *J. Chem. Phys.* **153**, 144204 (2020).

MO 9.4 Wed 11:15 MO-H5

Tracking Ultrafast Exciton Diffusion in Squaraine Polymers

at Various Temperatures — ●SIMON BÜTTNER¹, JULIAN LÜTTIG¹, PAVEL MALÝ^{1,2}, ARTHUR TURKIN³, CHRISTOPH LAMBERT³, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czech Republic — ³Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Exciton diffusion is an important process in solar light harvesting and organic electronics. We use exciton-exciton-interaction two-dimensional (EEI2D) spectroscopy [1], which observes the process of exciton-exciton annihilation (EEA) to track the exciton diffusion in organic materials. Using EEI2D spectroscopy, we recently found in squaraine polymers a change from wavelike transport to a sub-diffusive character of exciton diffusion on an ultrafast timescale [2]. For further investigations we now analyzed the influence of the environment on exciton diffusion. We embedded the squaraine polymers in a polystyrene matrix and used EEI2D spectroscopy in a cryostat to determine the effect of temperature on exciton diffusion. We also compare the results with temperature-dependent measurements on squaraine polymers in solution to demonstrate the differences between a solid and a liquid environment.

[1] J. Dostál et al., *Nat. Commun.* **9**, 2519, (2018)

[2] P. Malý et al., *Chem. Sci.* **11**, 456 (2020)

MO 9.5 Wed 11:30 MO-H5

Dynamics of photoexcited Cs atoms attached to helium nanodroplets — ●NICOLAS RENDLER¹, AUDREY SCOGNAMIGLIO¹, MANUEL BARRANCO^{2,3,4}, MARTI PÍ^{2,4}, NADINE HALBERSTADT³, KATRIN DULITZ¹, and FRANK STIENKEMEIER¹ — ¹Institute of Physics, University of Freiburg, Germany — ²Departament FQA, Universitat de Barcelona, Spain — ³IRSAMC, Université de Toulouse, France — ⁴IN2UB, Universitat de Barcelona, Spain

We present an experimental study of the dynamics of photoexcited Cs atoms located in a dimple on the surface of He nanodroplets. The repulsive interaction between the electronically excited alkali atom and the He environment usually leads to the ejection of the excited alkali atom from the surface of the He nanodroplet [1]. This process can be accompanied by fast electronic relaxation induced by the He environment and by the formation of He-Cs exciplex molecules [2]. After ionization, alkali atoms tend to be attracted by the He nanodroplet which eventually leads to their solvation inside of the droplet interior. Using femtosecond pump-probe spectroscopy combined with velocity-map-imaging and ion-time-of-flight detection, we have determined the time scales for Cs atom ejection and solvation after excitation to the 6p state as well as for CsHe exciplex formation [3]. Our results are compared to results of density-functional-theory simulations [4]. [1] M. Mudrich, F. Stienkemeier, *Int. Rev. Phys. Chem.* **33**, 301-339 (2014). [2] Reho et al., *Faraday Discuss.* **108**, 161, (1997). [3] N. Rendler et al., *J Phys Chem A.* **125** (41), 9048-9059 (2021). [4] Coppens et al., *Eur. Phys. J. D* **73**, 94, (2019).

MO 9.6 Wed 11:45 MO-H5

Ultrafast Dynamics of Xanthine Derivatives and their Use in a Nickel-Catalysed Cross-Coupling Reaction — ●THOMAS RITTNER¹, RAFAEL E. RODRÍGUEZ-LUGO², KARINA HEILMEIER¹, SVENJA WORTMANN¹, SIMON DIETZMANN², ROBERT WOLF², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg

Carbon-carbon and carbon-heteroatom cross-coupling is of high relevance in organic synthesis. In recent years, photo-induced nickel dual-catalysis has been successfully implemented for such bond-forming reactions under exceptionally mild conditions, albeit usually expensive precious metal containing photosensitizers are required [1]. We circumvent this issue with newly developed Xanthine-based ligands.

We employ both stationary and time-resolved absorption and emission spectroscopy to unveil the mechanism of this newly developed catalytic system. Spectral properties and dynamics of the ligands, of the reaction mixture, and of a model complex are juxtaposed. The coordination of the Xanthine ligands to Ni(II) is found to be rather weak. The lack of spectral overlap of ligand absorption and light source, as well as

the ligand's short excited-state lifetime queries the direct involvement of the ligand in the primary photostep. We thus aim at identifying alternative mechanisms for the photocatalytic process. Additionally, a

competitive photoisomerization in the Xanthine ligand may occur.
[1] C. Zhu *et al.*, *Angew. Chem. Int. Ed.* **2021**, *60*, 17810.