

## A 9: Ultrafast Dynamics I (joint session MO/A)

Time: Tuesday 11:00–13:00

Location: F102

## Invited Talk

A 9.1 Tue 11:00 F102

**Revealing chiral charge migration in UV-excited molecules —**

•VINCENT WANIE<sup>1</sup>, ETIENNE BLOCH<sup>2</sup>, ERIK P. MÅNSSON<sup>1</sup>, LORENZO COLAIZZI<sup>1,3</sup>, SERGEY RYABCHUK<sup>3</sup>, KRISHNA SARASWATHULA<sup>1,3</sup>, ANDREA TRABATTONI<sup>1,4</sup>, VALÉRIE BLANCHET<sup>2</sup>, NADIA BEN AMOR<sup>5</sup>, MARIE-CATHERINE HEITZ<sup>5</sup>, YANN MAIRESSE<sup>2</sup>, BERNARD PONS<sup>2</sup>, and FRANCESCA CALEGARI<sup>1,3</sup> — <sup>1</sup>DESY, Germany — <sup>2</sup>Université de Bordeaux - CNRS - CEA, CELIA, France — <sup>3</sup>Universität Hamburg, Germany — <sup>4</sup>Leibniz Universität Hannover, Germany — <sup>5</sup>CNRS, France

Electron-driven charge migration occurs following photoexcitation of a molecule, leading to a charge density traveling rapidly along the molecular structure. We report our most recent works devoted to the investigation of charge migration in neutral molecules and its applications to manipulate the outcome of photochemical and photophysical processes. We exploited our new light source delivering few-femtosecond UV pulses in order to photoexcite below the ionization threshold and trigger electronic dynamics in chiral methyl-lactate. We used time-resolved photoelectron circular dichroism (TR-PECD) to image electronic coherences driving charge migration and disclose - for the first time - their impact on the molecular chiral response, allowing for an ultrafast chiroptical switching effect where the amplitude and direction of the photoelectron current generated by PECD can be controlled on a sub-10 fs timescale. The results provide important perspectives to exploit charge-directed reactivity for controlling the chiral properties of matter at the molecular scale. [1] V. Wanie et al., 'Ultrafast chiroptical switching in UV-excited molecules,' (under review, 2022).

A 9.2 Tue 11:30 F102

**UV and Mid-IR Photo-induced Dissociation Dynamics of Solvated (Bio)Molecular Complexes —**

•MUKHTAR SINGH<sup>1,2,3</sup>, MATTHEW SCOTT ROBINSON<sup>1,2,3</sup>, HUBERTUS BROMBERGER<sup>1,2</sup>, JOLIJN ONVLEE<sup>1,3</sup>, SEBASTIAN TRIPPEL<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Center for Ultrafast Imaging, Universität Hamburg — <sup>3</sup>Department of Physics, Universität Hamburg

We present the imaging of ultrafast UV- and thermal-energy-induced chemical dynamics of micro-solvated (bio)molecular complexes probed with strong-field ionization techniques [1]. We produce a pure gas-phase indole-water sample using a combination of a cold molecular beam and the electrostatic deflector [2]. To study the induced dynamics, we set up both a UV and a mid-IR pump-probe experiment, in which a 269 nm and 2.9  $\mu\text{m}$  laser pulses were used to excite the system, respectively. A 1.3  $\mu\text{m}$  laser pulses was used for ionizing the system. First experiments focused on the ion imaging of the UV and mid-IR-triggered systems. Furthermore, we will report on efforts to use laser-induced electron diffraction (LIED) [3,4] to probe the molecular dynamics to obtain structural information with atomic resolution.

[1] J Onvlee, *et al.*, *Nat Commun.*, DOI: 10.1038/s41467-022-33901-w

[2] S. Trippel, *et al.*, *Rev. Sci. Instrum.* **89**, 096110 (2018)

[3] J. Wiese, *et al.*, *Phys. Rev. Research* **3**, 013089 (2021)

[4] E. T. Karamatskos, *et al.*, *J. Chem. Phys.* **150**, 244301(2019)

A 9.3 Tue 11:45 F102

**Supramolecular dynamics investigated on hydrogen bonded pyrrole-water clusters upon site-specific x-ray photoionization —**

•IVO S. VINKLÁREK<sup>1</sup>, HUBERTUS BROMBERGER<sup>1</sup>, WUWEI JIN<sup>1</sup>, REBECCA BOLL<sup>2</sup>, MICHAEL MEYER<sup>2</sup>, SEBASTIAN TRIPPEL<sup>1</sup>, and JOCHEN KÜPPER<sup>1,3,4</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>European XFEL GmbH, Schenefeld — <sup>3</sup>Department of Physics, Universität Hamburg — <sup>4</sup>Center for Ultrafast Imaging, Universität Hamburg

Solvation of molecules crucially affects their photostability and opens additional pathways for the relaxation dynamics compared to isolated molecules. We intend to get molecular-level insight into the solvation effect in photofragmentation dynamics of a supramolecular system through our molecular beam experiments with stoichiometrically well-defined pyrrole-water (Pyr-H<sub>2</sub>O) clusters [1]. Concretely, the dissolution dynamics of the spatially separated pure sample of Pyr-H<sub>2</sub>O clusters prepared by the electric deflector was investigated through an IR-pump-x-ray-probe experiment. The singly ionizing IR-pulse triggers

the (Pyr-H<sub>2</sub>O)<sup>+</sup> fragmentation, which is then site-specifically probed by x-ray free-electron laser pulses [2] at different times of the pyrrole-H<sub>2</sub>O separation. The study of the hydrogen-bound Pyr-H<sub>2</sub>O system is especially relevant to abundant pyrrole-containing biomolecules and establishes a novel approach for investigating the key role of intermolecular interactions in supramolecular dynamics.

[1] Johny, M. et al. *Chem. Phys. Lett.*, **2019**, 721, 149-152. [2] Onvlee, J. et al., *Nat. Commun.*, in press, arXiv:2103.07171 [physics]

A 9.4 Tue 12:00 F102

**Real time tracking of ultrafast dynamics in liquid water —**

•GAIA GIOVANNETTI<sup>1</sup>, AMMAR BIN WAHID<sup>1</sup>, SERGEY RYABCHUK<sup>1</sup>, HUI-YUAN CHEN<sup>2</sup>, VINCENT WANIE<sup>1</sup>, ANDREA TRABATTONI<sup>1,3</sup>, ERIK MAANSSON<sup>1</sup>, HUGO MARROUX<sup>4</sup>, MAJED CHERGUI<sup>2</sup>, and FRANCESCA CALEGARI<sup>1,5</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Notkestr. 85, 22607 Hamburg, Germany — <sup>2</sup>Ecole Polytechnique Fédérale de Lausanne, Rte Cantonale, 1015 Lausanne, Switzerland — <sup>3</sup>Institute of Quantum Optics, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover, Germany — <sup>4</sup>Laboratoire Interactions, Dynamiques et Lasers, CEA-Saclay, 91191 Gif-sur-Yvette, France — <sup>5</sup>The Hamburg Centre for Ultrafast Imaging, Universität Hamburg, 22761 Hamburg, Germany

Understanding the properties of water is key to determinate the effects of the liquid environment on the dynamics of biological systems. In our experiment, a 3 fs visible pump impulsively creates a vibrational wave-packet, whose evolution is probed by a time-delayed sub-2 fs UV pulse [1]. As a result of the wave-packet dynamics, the probe signal is modulated in time and the vibrational spectrum can be obtained by a Fourier analysis of the temporal interferogram. A preliminary analysis of our data shows a transient signal whose oscillation period (~11 fs) and decay time (~70 fs) match the values expected for the O-H stretching mode in the ground electronic state of liquid bulk water [2]. Further theoretical insights will allow us to assign specific contributions from the ground, excited and ionized states. [1] Opt. Lett. **44**, 1308-1311 (2019) [2] J. Chem. Phys. **135**, 244503 (2011).

A 9.5 Tue 12:15 F102

**Systematic variation of triplet chromophore energies in iron(II) complexes linked to organic chromophores —**

•MORITZ LANG<sup>1</sup>, PHILIPP DIERKS<sup>2</sup>, MIGUEL ARGÜELLO CORDERO<sup>1</sup>, MATTHIAS BAUER<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institute for Physics, University of Rostock, Germany — <sup>2</sup>Faculty of Science, CSSD, Paderborn University, Germany

For the efficient conversion of solar light, photosensitizers with appropriate absorption properties and long living excited states are crucial. Iridium and ruthenium complexes stand out due to their extraordinary stable triplet metal-to-ligand charge transfer (3MLCT) excited states but are expensive and toxic. To find sustainable alternatives, iron-based metal complexes are intensely studied. But due to an efficient internal conversion pathway mediated by metal centered states, the MLCT lifetime and therefore the performance of these types of complexes are still limited. In a systematic study the influence of various chromophores attached to homoleptic iron complexes was investigated. The excited state dynamic was studied by ultrafast transient absorption spectroscopy. For particular chromophores an additional decay component was observed, exceeding the lifetime of the otherwise predominant 3MLCT state by an order of magnitude. With fitting energy levels, a triplet state of the chromophore is populated during the relaxation process, achieving a comparably stable intermediate configuration. A better understanding and further improvement of these systems will contribute to the ultimate goal of developing efficient iron based photosensitizers for solar energy conversion.

A 9.6 Tue 12:30 F102

**Ultrafast dynamics of photochemical nitrile imine formation —**

•STEFAN FLESCH and PETER VÖHRINGER — Clausius-Institut für Physikalische und Theoretische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Wegelerstr. 12, D-53115 Bonn

The chemical reactivity of nitrile imines is of great utility in organic synthesis with applications rapidly expanding into the materials and life sciences.<sup>1</sup> Yet, our understanding of the electronic and molecular structures of nitrile imines remains incomplete and the elementary

mechanism of their photoinduced generation is entirely unknown. Here, femtosecond infrared spectroscopy after 266 nm-excitation of 2,5-diphenyltetrazole has been carried out to temporally resolve the formation and structural relaxation dynamics of the nascent diphenyl-nitrile imine in liquid solution under ambient conditions.<sup>2</sup> An initial sequence of intersystem crossings within 250 fs is followed by the cleavage of N<sub>2</sub> with formation of a structurally relaxed nitrile imine on the adiabatic ground-state singlet surface within a few tens of picoseconds. The infrared spectrum supports the notion of a "floppy" nitrile imine molecule whose equilibrium character ranges from fully propargylic to fully allenic under these conditions.

## References:

- 1 G. Bertrand, C. Wentrup, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 527-545.  
2 S. Flesch, P. Vöhringer, *Angew. Chem. Int. Ed.* **2022**, e202205803.

A 9.7 Tue 12:45 F102

**Investigating the oxidation states of a perylene bisimide cyclophane with ultrafast spectroelectrochemistry** — •REBECCA FRÖHLICH<sup>1</sup>, JESSICA RÜHE<sup>2</sup>, MICHAEL MOOS<sup>2</sup>, FRANK WÜRTHNER<sup>2</sup>, CHRISTOPH LAMBERT<sup>2</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 Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

From photosynthesis to optoelectronic devices, charged species fulfill essential roles in our everyday world. With spectroelectrochemistry the oxidation states of molecules can be generated and investigated under potential control. In our setup we combine spectroelectrochemistry with femtosecond transient absorption spectroscopy to investigate the dynamics of charged species on an ultrafast timescale [1].

Here we show new data on the oxidation states of a perylene bisimide cyclophane [2]. A fit of the cyclic voltammetry data of the molecule shows four reduction steps with closely lying redox potentials. The four reduced states show a change in absorption which is highlighted by the deconvolution of the absorption spectroelectrochemistry data. Through the fits of the absorption spectra the charged species can be distinguished in a set of transient absorption spectroelectrochemistry maps. The excited state lifetimes of the reduced molecule are analyzed with global fitting and change according to their oxidation state.

[1] J. Heitmüller et al., *Spectrochim. Acta Part A*, *253*, 119567 (2021)

[2] J. Rühle et al., *Organic Materials*, *2*, 149-158 (2020)