O 104: Focus Session: Ultrafast Processes in Organic Semiconductors and Perovskites III (joint session O/CPP)

Time: Friday 10:30–11:45 Location: MA 004

O 104.1 Fri 10:30 MA 004

Unveiling ultrafast vibronic dynamics in organic chromophores from first principles — •Michele Guerrini[1], Jannis Krumland[1,2], and Caterina Cocchi[1,2] — [1]Physics Department and Center for Nanoscale Dynamics(CeNaD), Carl von Ossietzky Universität Oldenburg, Germany — [2]Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Identifying and quantifying the interplay between electron and nuclear dynamics in the excited state of organic molecules is of paramount importance to unveil and interpret their complex photophysics upon ultrafast excitation. In this work, we investigate from first principles the ultrafast vibronic dynamics of p-coumaric acid chromophore [1]. We start off the simulations in excited states corresponding to bright or dark transitions. By monitoring the kinetic energy spectral density [2] and the population dynamics, we analyze the characteristics of the electron-nuclear motion and its evolution over a time window of 300 fs. We observe that anharmonic and non-adiabatic effects are particularly pronounced in excitations with charge-transfer character and lead to instabilities with the eventual distortion of the system. On the other hand, the dynamics initialized from bright excited states with delocalized character remains electronically and structurally stable, and the resulting nuclear motion is markedly harmonic.

[1] Theor. Chem. Acc. 142, 110 (2023)
[2] J. Phys. Chem. A, 125, 9619 (2021)

O 104.2 Fri 10:45 MA 004

Ultrafast Charge-Transfer in Spiro-Bridged Triphenylamine Derivatives Investigated by Broadband Transient Absorption Spectroscopy — •Danyellen Galindo[1], Angelina Jocic[2], Anna Weidlich Weidlich[3], Frank Rominger[2], Thomas Oeser[2], Jonathan Zerhoch[1], Felix Deschler[1], Andreas Drew[3], Milan Kivala[2], and Tiago Buckup[1] — [1]PCI, Universität Heidelberg, Heidelberg — [2]OCI, Universität Heidelberg, Heidelberg — [3]IWR, Universität Heidelberg, Heidelberg

Triphenylamine compounds (TPA) are studied in order to understand their photochemical processes such as charge transfer (CT). This investigation is motivated by their ability in stabilizing positive charges through a delocalize π-system, thereby facilitating hole transport. This work aimed to study the optical properties of Spiro-bridged Fluorene N-heterotriangulenes (FTN-H) and FTN-(CN)6. Both compounds, dissolved in dichloromethane (DCM), underwent transient absorption experiments with 300 nm excitation. Initial findings suggest that the solvent does not play a significant role in the CT process. The non-subsituted compound upon excitation simultaneously displayed S1 electronic band for the molecule core and fluorene side group, succeeded by a 2 ns inter-system crossing (ISC) transition, thus forming a triplet state T*1 that decays to S0 with time constant of 16 *s. FTN-(CN)6 exhibited overall comparable dynamics, but also displayed an ultrafast CT between S1 and T*1 states. Such CT, which can be observed in various donor-acceptor materials, hints at potential applications in solar energy conversion and storage systems.

O 104.3 Fri 11:00 MA 004

The effect of the acceptor strength on intramolecular charge separation in quadrupolar dye — •Somayeh Souri[1], Katrin WInte[1], Daniel Luenemann[1], Fulu Zheng[2], Mohamed Madjet[2], Teresa Kraus[3], Elena Mena-Osteritz[3], Peter Baeuerle[3], Sergei Tretiak[4], Antonietta De Sio[1], and Christoph Lienau[1] — [1]Oldenburg University, Germany — [2]Bremen University, Germany — [3]Ulm University, Germany — [4]Los Alamos National Laboratory, USA

Quadrupolar dyes, consisting of two terminal acceptors (A) linked to a central donor (D) are of high relevance for applications in nonlinear optics and photovoltaics. They recently demonstrated exceptional nonadiabatic quantum dynamics. In A-D-A thin films, we have uncovered the existence of intermolecular conical intersections, funneling energy into a lower-lying electronic state within less than 50 fs [1]. This raises the question how the strength of the acceptor group affects the quantum dynamics. Chemical intuition suggests that an increase in acceptor strength may accelerate charge transfer and increase its yield. We synthesize three A-D-A molecules with different acceptor strength and study them in polar solvents using ultrafast spectroscopy with 10fs time resolution. Even though we can distinguish between vibronic coupling-induced charge separation on a sub-100 fs scale and slower solvatochromism, we observe only weak effects of the acceptor group on the dynamics. The results suggest that vibronic coupling-induced excited state symmetry breaking plays a major role in quantum dynamics. [1] A. De Sio et al., Nature Nano 16, 63 (2021).

O 104.4 Fri 11:15 MA 004

Probing Site-Specific Photocatalytic Activity of Triazin-Based Graphitic Carbon Nitride via Time-Resolved and Resonant X-Ray Photoelectron Spectroscopy. — •Matz Nissen[1], Charlotte Ruhmlieb[1], Ivan Baev[1], Sebastian Denke[1], Lukas Wenthaus[3], Dmytro Kutnyakhov[3], Nils Wind[2,3], Federico Pressacco[3], Jens Buck[2], Steffen Palutke[4], Marion Kuhlmann[3], Günter Brenner[3], Kai Rossnagel[2,3], Alf Mews[1], and Michael Martins[1] — [1]Universität Hamburg, D — [2]Christian-Albrechts-Universität zu Kiel, D — [3]DESY, Hamburg, D — [4]European XFEL, Hamburg, D

Triazin-Based Graphitic Carbon Nitride (TGCN) has shown potential as a metal-free catalyst for photocatalytic water splitting, utilizing soley a visible light source and water. To gain further insight into the morphology of TGCN and the specific location where water binds during the catalytic reaction, we conducted resonant and time-resolved photoelectron spectroscopy of the carbon and nitrogen sites in a clean and a water environment. These experiments were done at beamline P04 of PETRAIII and beamline PG2 of FLASH respectively. Altering the sample environment shows differences in the resonant maps of the N K-edge. Additionally, time resolved measurements showed an excitation in the nitrogen spectra, specifically in the ring structure of the graphitic system. These results aim to help to improve the catalytic performance of the sample.

O 104.5 Fri 11:30 MA 004

Ultrafast dynamics in polymeric carbon nitride thin films probed by time-resolved extreme-ultraviolet photoemission spectroscopy — Nataliia Kuzkova[1,2], Igor Yu. Kiyan[1], Iain Wilkinson[1], and •Christoph Merschjann[1] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — [2]Advanced Research Center for Nanolithography, Science Park 106, 1098 XG Amsterdam, The Netherlands

Polymeric carbon nitrides (PCN) have been extensively studied for various possible applications, mainly in the field of photocatalysis, but also as potential organic semiconductors, luminescent materials, etc. Especially photocatalytic applications are affected by the apparently low charge-separation and transport efficiency of PCN. It is therefore of interest to investigate the early-time dynamics of photoexcited charge carriers, specifically at the surface of the photocatalyst. To this end, we applied femtosecond time-resolved pump-probe extreme-ultraviolet photoemission spectroscopy (TRPES) to differently synthesized PCN thin films. Excitation at 400 nm sequentially populates a pair of short-lived transient species, which subsequently produce two different long-lived excited states on a sub-picosecond time scale. These could be assigned to singlet-exciton and charge-transfer states with a high initial spatial correlation, respectively. The results also show the potential of TRPES as a tool for in-situ investigations of early-time dynamics in photocatalytic processes.

[1] Kuzkova et al., *Phys. Chem. Chem. Phys.*, **25**, 27094 (2023)