CPP 13: Molecular Electronics and Excited State Properties I

Time: Monday 17:15–18:30 Location: H38

CPP 13.1 Mon 17:15 H38

Revealing the Origin of low-energy Excited State Absorption in the nonlinear Optical Properties of Thiophene — •Mustapha Driouech, Michele Guerrini, and Caterina Cocchi — Carl von Ossietzky Universität Oldenburg

Optical nonlinearities in organic molecules are useful for advanced applications. Among them, optical limiting is particularly relevant to prevent critical damage to the human eyes and artificial sensors from intense radiation. In this ab initio study, we investigate the nonlinear optical properties of thiophene oligomers with a non-perturbative approach based on real-time time dependent density functional theory [1]. We study the optical absorption spectra obtained after applying a broadband instantaneous electric field. For sufficiently high intensities, we observe the appearance of absorption peaks at low energies that are not present in the linear spectra. To investigate in more details the nonlinear mechanisms involved, we perform pump-probe simulations combined with analysis of the population dynamics revealing that the emerging features are due to excited state absorption in the visible region. Our results show that this fully ab initio methodology is able to capture and unravel the fundamental mechanisms of optical nonlinearities in organic molecules.

[1] C. Cocchi, et al., Phys. Rev. Lett. 112, 198303 (2014).

CPP 13.2 Mon 17:30 H38

Theoretical perspectives on ground- and excited state absorption in organic materials: comparing TDDFT, GW/BSE, and post-Hartree-Fock methods — •Narges Taghizade[1], Andreas Windischbacher[1], Andreas W. Hauser[2], and Peter Puschnig[1] — [1]Institute of Physics, University of Graz, Austria — [2]Institute of Experimental Physics, Graz University of Technology, Austria

Ground- and excited-state absorption (ESA) properties of conjugated organic materials are fundamental to the development of advanced optoelectronic devices. In this contribution, we specifically focus on molecules, which pose challenges to traditional theoretical approaches owing to significant electron correlation resulting in complex charge transfer and multi-reference characteristics, particularly when it comes to excited state properties. To address these complexities, we compute the ground and ESA spectra using a number of complementary, advanced theoretical methods. First, we employ time-dependent density functional theory within the linear and quadratic response frameworks, respectively. Second, we present results from a GW/BSE many-body perturbation theory approach thereby addressing the challenge of accurately accounting for charge transfer excitations. Third, we also apply post-Hartree-Fock methods, such as the multi-configurational self-consistent field method in order to tackle the strong electron correlation and multi-reference effects. The comparison of our results highlights the strengths and limitations of various computational approaches and offers a pathway toward improved theoretical models for the design of efficient optoelectronic materials.

CPP 13.3 Mon 17:45 H38

Charge and energy transfer mechanisms in a singlet fission donor-acceptor complex — •Karin S. Thalmann[1], Johan E. Runeson[1], Pedro B. Coto[2], and Michael Thoss[1] — [1]Institute of Physics, University of Freiburg, Germany — [2]Spanish National Research Council (CSIC), Madrid, Spain

Singlet fission is a photophysical process transforming a singlet excited electronic state to two triplet states [1]. Thus, materials exhibiting singlet fission have the potential to increase the efficiency of solar cells. Adding an acceptor to a singlet fission active molecule enables the extraction of charges and excitation energy. In our work, we study a diazadiborine dimer as donor [2] and tetracyanoquinodimethane as acceptor molecule. Using *ab initio* multireference perturbation theory calculations, we build a vibronic model Hamiltonian and further perform quantum dynamical [3] and mixed quantum-classical simulations [4] to analyse the charge and energy transfer dynamics in the complex. With our techniques, we characterise competing charge and energy transfer processes as well as intramolecular and intermolecular singlet fission. The analysis reveals the role of the different electronic states and vibrational modes in the dynamics of the donor-acceptor complex.

[1] M. B. Smith *et al.*, *Chem. Rev.* **110**, 6891-6936 (2010).
[2] T. Zeng, *J. Phys. Chem. Lett.* **7**, 4405-4412 (2016).
[3] S. R. Reddy *et al.*, *J. Phys. Chem. Lett.* **9**, 5979-5986 (2018).
[4] J. E. Runeson *et al.*, *J. Chem. Phys.* **159**, 094115 (2023).

CPP 13.4 Mon 18:00 H38

The Influence of Solvent Nature and Annealing Conditions on the TADF Properties of DMAC-TRZ in Films and Single Crystals — •Anatolii Kuimov[1], Sergey Bagnich[1], Christopher Greve[2], Eva M. Herzig[2], and Anna Köhler[1] — [1]Soft Matter Optoelectronics, University of Bayreuth, Germany — [2]Dynamik und Strukturbildung - Herzig Group, Universität Bayreuth, Germany

We investigated the impact of molecular arrangement and post-processing conditions on the thermally activated delayed fluorescence (TADF) of the donor-acceptor type molecule DMAC-TRZ. Specifically, we studied luminescence at various temperatures and time delays after excitation across different solid-state morphologies, including amorphous films, polycrystals, and single crystals, complemented by X-ray analysis of the single crystal. In single crystals, we observed that emission energy, the singlet-triplet gap, and TADF intensity were influenced by processing conditions, such as aging, thermal and solvent annealing, and the choice of solution for crystal growth. These effects are attributed to changes in the torsion angle between the donor and acceptor moieties. Comparisons with polycrystals and amorphous films reveal that introducing morphological disorder promotes a more orthogonal donor-acceptor arrangement, leading to a smaller singlet-triplet gap and enhanced TADF. Our findings emphasize the pivotal role of molecular conformation in modulating photophysical properties. This study highlights the potential of tailoring material performance through structural modifications and annealing strategies to optimize TADF efficiency for organic optoelectronic applications.

CPP 13.5 Mon 18:15 H38

Effect of Junction Structure on Quantum Interference in Single-Molecule Junctions — •Aoshi Yamane, Shintaro Fujii, and Tomoaki Nishino — Department of Chemistry, School of Science, Institute of Science Tokyo, 2-12-1 Ookayama, Meguro-ku, Tokyo, Japan

The destructive quantum interference (DQI) effect in single-molecule junctions induces a steep decrease in electron transmission at specific energies, enables high on/off ratios of electrical conductivity, and is expected to be applied to molecular devices such as transistors and switches. Here, we aimed to elucidate the effects of molecular and molecule/metal interface structures on DQI. We focused on disubstituted naphthalene with different types and positions of anchoring groups connecting molecules and electrodes. Break junction measurements of the molecular junctions demonstrated that for naphthalenedithiol (NDT), 2,7-NDT showed significantly lower conductivity compared to 2,6-NDT, indicating the presence of DQI in 2,7-NDT. On the other hand, for naphthalenedicarbonitrile (NDCN), 2,6-NDCN and 2,7-NDCN showed similar conductance. Combined with Flicker noise analysis and DFT-NEGF transmission calculations, we demonstrate that the DQI features in 2,7-NDCN are masked by the contribution of electrode-π coupling, which short-circuit the molecular junctions. The present study provides important insights into the control of unique electron transport properties induced by DQI in single-molecule junctions.