

## CPP 20: Molecular Electronics and Excited State Properties II

Time: Monday 15:00–16:15

Location: ZEU 260

CPP 20.1 Mon 15:00 ZEU 260

**Modeling the Complex Band Structure of Conjugated Polymers via Kronig-Penney-like Models** — ●FLORIAN GÜNTHER<sup>1</sup>, KEVIN PREIS<sup>2</sup>, and SIBYLLE GEMMING<sup>2,3</sup> — <sup>1</sup>Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, Brazil — <sup>2</sup>Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany — <sup>3</sup>Institut für Ionenstrahlphysik und Materialforschung, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

In molecular electronics, it is crucial to understand and control the electronic properties of the involved materials. Due to the small length scale, which is in the range of nanometers and below, the coherent electron tunneling plays an important role in the conduction behavior of the used compounds. Its exponential decay with the length can be studied by considering the complex band structure in the region of the Fermi energy.

In our work, we calculate the real and the complex bands of various conjugated polymers using the density functional based tight binding approach. The results are fitted with the analytical solutions arising from the two-band tight binding and the Kronig-Penney models. While the former exhibits less free parameters, the latter is able to reproduce the non-symmetric shape of the complex bands with respect to the Fermi energy. We found that the product of the barrier height and width of the Kronig-Penney model correlates with the tunneling inverse decay length. Our results suggest that the coherent electron tunneling through conjugated polymers can be estimated by fitting the Kronig-Penney model to the real band structure.

CPP 20.2 Mon 15:15 ZEU 260

**Understanding Ultrafast Proton transfer reaction in Molecular Crystals** — ●HYEIN HWANG<sup>1,2</sup>, VANDANA TIWARI<sup>1,2</sup>, SIMON BITTMANN<sup>1</sup>, HONG-GUANG DUAN<sup>1</sup>, FRIEDJOF TELLKAMP<sup>1</sup>, AJAY JHA<sup>1</sup>, and R. J. DWAYNE MILLER<sup>1,3</sup> — <sup>1</sup>MPSD, Hamburg, Germany — <sup>2</sup>Department of Chemistry, University of Hamburg, Germany — <sup>3</sup>Departments of Chemistry and Physics, University of Toronto, Canada

Ultrafast proton transfer reactions is a topic of great interest particularly due to their association with the understanding of primary elementary reaction pathways in functional electrochemical and biological systems. Although these reactions have been extensively investigated in solution for the role of interaction between the solute and the solvent-bath, but the reaction dynamics in bulk single molecular crystals remains elusive. Here, we study ultrafast intramolecular proton transfer reaction in hydroxyanthraquinones in crystalline form, where molecular system forms the lattice. We use ultrafast transient absorption studies complemented with quantum chemistry calculations to reveal the role of spatial arrangement of the reactants within the lattice in reaction dynamics. Our work highlight the importance of intermolecular interactions guiding ultrafast dynamics in crystals.

CPP 20.3 Mon 15:30 ZEU 260

**Exciton dynamics in optically active surface-mounted metal-organic frameworks: A time-resolved second harmonic generation study** — ●VIPILAN SIVANESAN<sup>1</sup>, RITESH HALDAR<sup>2</sup>, CHRISTOF WÖLL<sup>2</sup>, and PETRA TEGEDER<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Universität Heidelberg, Germany — <sup>2</sup>Institute of Functional Interfaces, Karlsruhe Institute of Technology, Germany

For the optimization of organic optoelectronic devices it is important to understand the ultrafast electronically excited state dynamics in organic semiconductors after optical excitation. For instance, different molecular packing and relative orientations of the optically ac-

tive chromophores can affect the excitonic coupling strength. This can be studied in crystalline molecular assemblies by integrating these chromophores into surface-mounted metal-organic frameworks (SUR-MOFs) as organic linkers. Varying the side-groups of the molecules enables to engineer the crystal structure to tune the excitonic coupling. To analyse the influence of this crystal engineering on the ultrafast dynamics we investigated thin films of chromophore functionalized Zn-SURMOF by means of femtosecond time-resolved second harmonic generation.

Literature: [1] R. Haldar et al., *Chem. Eur. J.*, **23**, 14316 (2017) [2] R. Haldar et al., *Nature Commun.* **10**:2048 (2019)

CPP 20.4 Mon 15:45 ZEU 260

**Optical absorption of azobenzene-derivatives in solution and in metal-organic frameworks via embedded orbital-tuned Bethe-Salpeter calculations** — ●ASEEM RAJAN KSHIRSAGAR and ROBERTA POLONI — Univ. Grenoble-Alpes, CNRS, Grenoble-INP, SIMaP, Grenoble 38000, France

The use of UV-Vis light has been proposed as an energy-efficient strategy for capture and release of CO<sub>2</sub> in azobenzene-functionalized metal-organic frameworks (MOFs). We recently demonstrated that the mechanism behind the observed reversible change in gas adsorption is metal-node blocking by the *cis* isomer upon UV-Vis excitation [1]. Large photo-isomerization yields are needed in order to achieve large changes in CO<sub>2</sub> uptake, underlining the importance of a highly selective optical absorption by each isomer. For this, the Bethe-Salpeter formalism with a non-equilibrium embedding scheme has been employed to accurately compute the paradigmatic case of S<sub>1</sub> band separation between *cis* and *trans* in azobenzene derivatives in solution. Besides embedding, we show that the choice of the DFT functional is critical, despite the iterative convergence of *GW* quasiparticle energies. In light of this result, we employ an environment-consistent orbital-tuning method to study 20 azobenzene derivatives in solution and then extend this approach to study the nature of the lowest energy excitons of MOF and the implications of using periodic versus non-periodic models of MOFs. [1] Yang, Kshirsagar, Eddin, Lin, Poloni, *Chem. Eur. J.* **24**, 15167 (2018); [2] Kshirsagar, D'Avino, Blase, Li, Poloni, *ChemRxiv* (2019), url: <https://chemrxiv.org/s/a7791c5ab68368b15dce>.

CPP 20.5 Mon 16:00 ZEU 260

**Two-dimensional electronic spectroscopy of phthalocyanine on rare gas clusters** — ●ULRICH BANGERT, LUKAS BRUDER, MARCEL BINZ, FRIEDEMANN LANDMESSER, ELENA LEISSLER, DANIEL UHL, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

With the recent advances of two-dimensional electronic spectroscopy (2DES) towards the gas phase, versatile samples like rare gas cluster beams become accessible [1]. Doping rare gas clusters with multiple molecules yields well defined many body systems. These systems are comparable to highly dilute thin film, however feature weak interaction with the substrate and are cooled down to  $\leq 10$  K. In previous experiments, such systems provided valuable details about singlet fission and super radiance in acene molecules [2,3]. We now apply for the first time 2DES to this approach and study free-base phthalocyanine in different environments: embedded in superfluid helium nanodroplets, deposited on the surface of neon clusters and as a thermal vapor. We find distinct differences in the photodynamics of the molecular assemblies.

[1] L. Bruder et al., *J. Phys. B: At. Mol. Opt. Phys.* **52** 183501 (2019).

[2] S. Izadnia et al., *J. Phys. Chem. Lett.* **8**, 2068 (2017).

[3] M. Müller et al., *Phys. Rev. B* **92** (12), 121408 (2015).