

CPP 12: Molecular Electronics and Excited State Properties I

Time: Monday 16:15–17:30

Location: H 0106

CPP 12.1 Mon 16:15 H 0106

Charge transfer dynamics in singlet fission donor-acceptor complexes — ●KARIN S. THALMANN¹, PEDRO B. COTO², and MICHAEL THOSS¹ — ¹Institute of Physics, University of Freiburg, Germany — ²Spanish National Research Council (CSIC), Madrid, Spain

Singlet fission (SF) is a spin-allowed process in organic materials, which generates two triplet excitons from a singlet exciton [1]. Therefore, materials exhibiting SF are potential candidates to improve solar cells to achieve efficiencies beyond the Shockley-Queisser limit [2,3]. To be able to harvest electrons, an acceptor is added to the SF molecule. Specifically, we examine the complex of a diazadiborane dimer [4] as donor and tetracyanoquinodimethane as acceptor molecule. Using ab-initio multireference perturbation theory, we analyse the electronic structure, which includes charge transfer and multiexcitonic states between the donor and acceptor molecule. Moreover, we perform quantum dynamical simulations using a vibronic model Hamiltonian to investigate the charge transfer dynamics from the donor to the acceptor molecule. Furthermore, we investigate the influence of individual modes on the dynamics.

- [1] M. B. Smith, J. Michl, *Chem. Rev.* **110**, 6891 (2010).
 [2] W. Shockley, H. J. Queisser, *J. Appl. Phys.* **32**, 510 (1961).
 [3] A. J. Baldacchino et al., *Chem. Phys. Rev.* **3**, 021304 (2022).
 [4] T. Zeng, *J. Phys. Chem. Lett.* **7**, 4405 (2016).

CPP 12.2 Mon 16:30 H 0106

Singlet Fission Born Quintet and Triplet States for Quantum Technologies — ●NITIK PANJWANI¹, KANAD MAJUMDER², WOONJAE KIM³, SOHAM MUKHERJEE⁴, JIEUN LEE³, K.C. KRISHNAPRIYA², JYOTISHMAN DASGUPTA⁵, ANDREW MUSSER⁴, SATISH PATIL², and ROBERT BITTL¹ — ¹Freie Universität Berlin, DE — ²Indian Institute of Science, IN — ³Yonsei University, KR — ⁴Cornell University, US — ⁵Tata Institute of Fundamental Research, IN

Molecular systems are promising candidates for quantum information technologies due to their reproducible nature and chemical tailorability. Photogenerated spin qubits are of interest as they form highly spin-polarised initial states e.g. in molecular systems undergoing singlet fission (SF), a process which can lead to both triplet and quintet states[1]. Furthermore, these states allow for optical detection[2] strategies to be implemented. We study a series of pentacene dimers with different linkers using electron paramagnetic resonance (EPR) spectroscopy. We investigate the role of linker geometry on relative spin state yields[3] and the influence of excitation wavelength on quintet sublevel populations[4]. Furthermore, we show how some dimers exhibit long-lived quintet states, examine the coherence properties, and investigate optical detectability in these dimers. Understanding the relationship between the spin properties and molecular structure will allow for realization of SF systems for quantum technologies.

- [1] L.R. Weiss et al, *Nature Phys.*, 2017, 13, 176 [2] G. Joshi et al, *J. Chem. Phys.*, 2022, 157, 164702 [3] K. Majumder et al, *J. Am. Chem. Soc.* 2023, 145, 20883 [4] W. Kim et al, arXiv:2304.05432, 2023

CPP 12.3 Mon 16:45 H 0106

Mapping Electronic Coupling in the Excited-State during Singlet Fission with Transient Two-Dimensional Electronic Spectroscopy — ●OSKAR KEFER¹, PAVEL V. KOLESNICHENKO¹, LUKAS AHRENS², JAN FREUDENBERG², UWE H. F. BUNZ², and TIAGO BUCKUP¹ — ¹PCI, Universität Heidelberg, Heidelberg — ²OCI, Universität Heidelberg, Heidelberg

Electronic coupling of an optically bright singlet- (S_1S_0) and a dark state, known as the correlated triplet pair ($^1[T_1T_1]$), is a driving factor for singlet fission (SF). Detailed insight into the nature of the coupling is gained from theoretical considerations, due to the challenging nature of experimental confirmation. Transient two-dimensional electronic spectroscopy (transient 2DES) can directly study electronic-state correlations of singlet- and triplet excitons by utilizing an actinic-pump

to launch SF beforehand.

We apply transient 2DES to spiro-linked SF-sensitizers, investigating the initial transformation of S_1S_0 to $^1[T_1T_1]$. Semi-quantum mechanical simulations allow extraction of relevant interaction parameters from measured cross-correlations of excited-states. Our findings indicate a direct SF-mechanism in the dimers, facilitated by non-adiabatic coupling between S_1S_0 and $^1[T_1T_1]$. A superposition of S_1S_0 and $^1[T_1T_1]$ is formed, which shifts towards $^1[T_1T_1]$, retaining the signatures of the coupled system even after completion. The experimental evidence reinforces the notion of the two interacting electronic states in equilibrium, a feat that was so far accessible only via computational methods.

CPP 12.4 Mon 17:00 H 0106

Ab-initio study on the effect of dipolar spin-spin interactions in singlet fission — ●R. K. KATHIR¹, PEDRO COTO², and MICHAEL THOSS¹ — ¹Institute of Physics, University of Freiburg, Germany. — ²Materials Physics Center (CFM), Spanish National Research Council (CSIC), Spain.

Interactions between triplet pair states are known to play a key role in important chemical processes. An example is singlet fission (SF), a photo-induced multiple exciton generation mechanism in which a singlet excited state transforms into a pair of triplet excitons [1]. Electron paramagnetic resonance experiments have provided evidence that this process involves the participation of singlet and quintet coupled triplet pair states [2,3,4]. In this contribution, we employ ab-initio multi-reference perturbation theory techniques to investigate the effect of the inter-triplet relative orientation, and the strength of the zero field splitting on the SF kinetics. We perform our studies on a series of modified pentacene dimers where the pentacene-like moieties are covalently bonded to a phenylene linker in ortho, meta, and para positions, shown to undergo intra-molecular SF [5]. Our results provide insight into the spin mixing in these systems, in particular regarding the fate of the coupled triplet pair state in SF.

References:

- [1] *Chem. Rev.*, 2010, 110, 6891-6936. [2] *Nat. Phys.*, 2017, 13, 176-181. [3] *Nat. Phys.*, 2017, 13, 182-188. [4] *Nat Commun.*, 2017, 8, 15171. [5] S. R. Reddy, et al., *J. Phys. Chem. Lett.*, 2018, 9, 5979-5986.

CPP 12.5 Mon 17:15 H 0106

Exploring the Mechanisms behind Non-Aromatic Fluorescence Using the DFTB Method — GONZALO DÍAZ MIRÓN¹, ●CARLOS R. LIEN-MEDRANO², DEBARSHI BANERJEE¹, URIEL N. MORZÁN¹, RALPH GEBAUER¹, and ALI HASSANALI¹ — ¹ICTP, Trieste, Italy — ²University of Bremen, Bremen, Germany

In contrast to our standard textbook spectroscopic intuition, which attributes the fluorescence in biological systems to aromatic or conjugated groups, there are intriguing cases where non-aromatic systems exhibit inherent absorption and fluorescence in the UV-visible range. Noteworthy examples include amyloid structures, individual non-aromatic amino acids and amino acids derivatives. This study aims to comprehensively evaluate the potential of the TD-DFTB method implemented in DFTB+ [1] to investigate the photophysics underlying non-aromatic fluorescence (NAF) phenomena. The focus is on amino-acid crystals, particularly L-glutamine and its chemically transformed counterpart, L-pyro-ammonium. By comparing TD-DFTB results to previous TD-DFT studies and experimental findings [2, 3], the research successfully demonstrates TD-DFTB's accuracy in capturing non-radiative decay pathways and fluorescence origins. Furthermore, TD-DFTB is utilized to explore environmental effects using a QM/MM approach, providing insights into the experimentally observed Stoke-Shift and revealing new nuances in non-radiative decay mechanisms.

- [1] Hourahine, B., et al. *JCP*, 152(12), 124101. (2020)
 [2] Stephens, A. D., et al. *PNAS*, 118(21).(2021)
 [3] Mirón, G. D., et al. *Nature Communications*, 14(1), 7325. (2023)