

# Charge transfer states in molecular and crystalline organics with PV and TADF applications

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Charge transfer (CT) states are important in molecular and condensed phase organic systems with technological applications. They form readily in  $\pi$ -stacked systems such as crystalline P3HT [1] or fullerene-polymer systems [2] with photovoltaic applications and donor-acceptor systems for thermally activated delayed fluorescence (TADF) applications [3]. They are nearly silent in linear optical spectroscopy because of the small ground state/CT state transition moment. Consequently they are typically populated by optical absorption to a higher state and relaxation via charge transfer from one polymer chain to a neighbour or between donor-acceptor fragments.

Electroabsorption (EA) spectroscopy is a nonlinear spectroscopy which measures the change in absorption caused by a static external electric field. It can be used to observe CT states through the interaction of the large excited state dipole moment and the external field. For symmetric dimer systems, CT states consist of even and odd combinations of configurations in which the electron and hole are on either half of the dimer. Splittings of these states are very small for complete charge transfer since the exchange integral is small. In contrast Frenkel excited states of symmetric dimers have larger exchange integrals and splittings. This results in well-known EA lineshapes for these states which are approximately the first and second derivatives of the linear optical absorption spectrum. The key requirement for the second derivative lineshape is the quasi-degeneracy of the odd and even pair of CT states.

EA spectra are calculated for a model donor-acceptor system using finite-field and third order electric susceptibility methods and found to be in excellent agreement. The latter approach is applied to tetrathiophene dimers and  $C_{60}$ -oligothiophene systems. CT states which are very weak in linear absorption have comparable strength to strong thiophene transitions in the third order susceptibility. CT states with technological importance typically lie below the main linear optical absorption lines and EA spectroscopy therefore offers a means of observing these states in experiment.

CI-singles calculations on crystalline P3HT show that CT states in which electron and hole are on neighbouring thiophene chains are low lying states of this system. This is a likely explanation for the 2-D conducting properties of polycrystalline P3HT films.

[1] *Charge transfer excitons in  $\pi$ -stacked thiophene oligomers and P3[Alkyl]HT crystals: CIS calculations and electroabsorption spectroscopy*, S.R. Sahoo and C. H. Patterson, J. Chem. Phys. 157, 074901 (2022)

[2] *Spectroscopic Identification of the Charge Transfer State in Thiophene/Fullerene Heterojunctions: Electroabsorption Spectroscopy from GW/BSE Calculations*, S.R. Sahoo and C. H. Patterson, J. Phys. Chem. C 127, 15928 (2023)

[3] *TDDFT versus GW/BSE methods for prediction of light absorption and emission in a TADF emitter*, D. Chaudhuri and C. H. Patterson, J. Phys. Chem. A, 126, 9627 (2022)