

## Origin of Space-separated Charges in Photoexcited Organic Heterojunctions on Subpicosecond Time Scales

Veljko Janković and Nenad Vukmirović

*Scientific Computing Laboratory, Centre for the Study of Complex Systems, Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia*

e-mail: veljko.jankovic@ipb.ac.rs

The promise of economically viable and environmentally friendly conversion of sunlight into electrical energy has driven vigorous and interdisciplinary research on donor/acceptor heterojunction organic photovoltaics. However, the actual mechanism of the emergence of free charges on subpicosecond (<100-fs) time scales following the excitation of a heterojunction remains elusive.

We investigate subpicosecond exciton dynamics in the lattice model of an all-organic heterojunction. Exciton generation by means of a photoexcitation, exciton dissociation, and further charge separation are treated on equal footing and on a fully quantum level using the density matrix formalism combined with the dynamics controlled truncation scheme [1]. Our results indicate that the space-separated charges appearing on <100-fs time scales following the photoexcitation are predominantly directly optically generated [2], in contrast to the usual viewpoint that they originate from ultrafast population transfer from initially generated excitons in the donor material. The space-separated states acquire nonzero oscillator strengths from donor excitons thanks to the strong resonant mixing between these two groups of exciton states. The results of ultrafast pump-probe experiments are commonly interpreted in terms of exciton populations only. Our theoretical insights into the ultrafast pump-probe spectroscopy highlight the importance of coherences, which cannot be disregarded on such short time scales, in the interpretation of pump-probe spectra [2].

### REFERENCES

- [1] V. Janković and N. Vukmirović, Phys. Rev. B 92, 235208 (2015).
- [2] V. Janković and N. Vukmirović, Phys. Rev. B 95, 075308 (2017).