Quantum dynamics of photoprocesses in extended molecular systems: coherence and correlations at the nanoscale

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The photophysics of extended systems like conjugated polymers or molecular aggregates is characterized on the one hand by the properties of the molecular building blocks and on the other hand by the delocalized nature of the electronic excitations, i.e., the formation of excitonic states. The dynamical phenomena induced by photoexcitation therefore involve an interplay of site-site interactions entailing excitation energy transfer (EET) and charge transfer (CT), and on-site vibronic coupling and trapping effects. Due to the prominent role of electron-phonon coupling, often accompanied by coherent dynamical effects on ultrafast time scales, an explicit quantum dynamical treatment is generally required. Our approach combines parametrized Hamiltonians, based on semiempirical and *ab initio* calculations, with accurate quantum dynamics simulations using the multiconfiguration time-dependent Hartree (MCTDH) method [1]. In addition, we employ transformation techniques [2,3] by which a relevant set of effective modes are constructed that allow for a hierarchical description of non-adiabatic dynamics in high-dimensional systems. Against this background, the talk will focus on coherent excitation transfer driven by torsional dynamics in poly-phenylene-vinylene (PPV) type systems [4], and on ultrafast exciton dissociation at polymer heterojunctions in fluorene-based TFB:F8BT blends [3] as well as at oligothiophene-fullerene junctions [5]. Particular consideration is given to the role of excitonic coherence *vs.* static and dynamic conformational disorder.

References

[1] G. A. Worth, H.-D. Meyer, H. Köppel, L. S. Cederbaum, and I. Burghardt, *Int. Rev. Phys. Chem.* **27**, 569 (2008).
[2] R. Martinazzo, B. Vacchini, K. H. Hughes, and I. Burghardt, *J. Chem. Phys.* (Comm.) **134**, 011101 (2011).
[3] H. Tamura, J. G. S. Ramon, E. R. Bittner, and I. Burghardt, Phys. Rev. Lett. **100**, 107402 (2008); I. Burghardt, E. R. Bittner, H. Tamura, A. Pereverzev, and J. G. S. Ramon, in: *Energy Transfer Dynamics in Biomaterial Systems*, Edited by I. Burghardt, D. A. Micha, E. R. Bittner (Springer, Heidelberg, 2009), *Chem. Phys. Ser.* **93**, 183.
[4] F. Sterpone, R. Martinazzo, A. N. Panda, and I. Burghardt, *Z. Phys. Chem.*, in press.
[5] H. Tamura, I. Burghardt, and M. Tsukada, *J. Phys. Chem. C,* in press.