

Mixed Quantum Classical Computation of Excitation Energy Transfer in Pheophorbide-a Complexes

Jörg Megow, Hui Zhu*, Zheng-wang Qu, Beate Röder, Volkhard May

Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany

**Institut für Mathematik, Freie Universität Berlin, Arnimallee 6, D-14195 Berlin, Germany*

The excitation energy transfer in a chromophore complex dissolved in ethanol is computed utilizing a mixed quantum classical methodology. The complex is formed by a butanediamine dendrimer to which four pheophorbide-a molecules are covalently linked. While all nuclear coordinates are described classically by carrying out room-temperature MD-simulations the electronic excitations are treated quantum mechanically utilizing a Frenkel-exciton model. We address two issues:

1. A new approach is introduced to directly include intramolecular vibrations from the MD-simulations into the former mixed quantum classical methodology. This approach shall be used to further improve the existing calculations of excitation energy transfer, linear absorbance and time- and frequency resolved emission spectra. Therefore the intramolecular vibrations are separated from the translation, rotation and low frequency chromophore oscillations for the full MD-trajectory by a complete analysis of all single atom trajectories. Thus translation, rotation and low frequency chromophore oscillations together define the so called reference structure. Making a harmonic approximation to the single atom positions in respect of the related reference structure atom positions using the Cartesian Hessian matrix elements given by HF-/CIS-calculations a highly fluctuating energy was calculated and added to the chromophore complex Hamiltonian.

2. The full quantum formula for the emission spectrum is translated into the mixed quantum classical case and time-resolved spectra up to 2 ns are computed. The chromophore complex excited state dynamics are described by the density matrix theory to account for both radiative and non-radiative decays. While the full emission spectrum only reflects excited state decay, the analysis of partial spectra reveals details of the excitation energy redistribution among the chromophores.

[1] H. Zhu and V. May: *Mixed Quantum Classical Simulations of Electronic Excitation Energy Transfer and Related Optical Spectra: Supramolecular Pheophorbide-a Complexes in Solution*, in I. Burghardt, V. May, D. A. Micha, and E. R. Bittner (eds.), Springer Series in Chemical Physics Vol. 93 (Springer-Verlag, 2009), p. 52

[2] H. Zhu, B. Röder and V. May: *Time and Frequency Resolved Spontaneous Emission from Supramolecular Pheophorbide-a Complexes: A Mixed Quantum Classical Computation*, Chem. Phys. 362, 19 (2009)