

## Photoinduced energy relaxation and redistribution in chlorophylls

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Optical properties of chlorophylls have drawn considerable attention because of their fundamental and biological relevance. Chlorophylls play an essential role in the conversion of sunlight into chemical energy in Green plants and various algae. Furthermore, they are also widely studied as candidates for molecular electronics applications. In this work, Non-Adiabatic Excited-State Molecular Dynamics simulations (NA-ESMD)[1] have been performed to study the internal conversion process in chlorophylls. We aim to achieve a detailed comprehension of the ultrafast intramolecular electronic and vibrational energy transfer that takes place after photoexcitation. Within our NA-ESMD framework, direct nonadiabatic molecular dynamics simulations can be applied to describe photoinduced dynamics in large organic conjugated molecules involving multiple coupled electronic excited states. Such NA-ESMD simulations are performed by combining the molecular dynamics with quantum transitions (MDQT) approach with “on the fly” analytical calculations of excited state energies, gradients, and non-adiabatic couplings terms. We present results of the intra- and intermolecular redistribution of the electronic transition density during the internal conversion process[2],[3]. Excited state trajectories are analyzed in terms of the ground state equilibrium normal modes[4]. Our analysis of the time evolution of the average mode energies uncovers that only a

small subset of the medium-to-high frequency normal modes actively participate in the electronic relaxation processes. These active modes are characterized by the highest overlap with the nonadiabatic coupling vectors (NACRs) during the electronic transitions. Further statistical analysis of the nonadiabatic transitions reveals that the electronic and vibrational energy relaxation occurs via two distinct pathways with significantly different time scales.

### References

- [1] “Nonadiabatic Excited-State Molecular Dynamics: Modeling Photophysics in Organic Conjugated Materials”, T. Nelson, S. Fernandez-Alberti, A. Roitberg, and S. Tretiak, *Accounts of Chemical Research*, 47(4), 1155-1164 (2014)
- [2] “Non-radiative relaxation of photoexcited chlorophylls: theoretical and experimental study”, W. P. Bricker, P. M. Shenai, A. Ghosh, M. Grace, M. Enriquez, P. H. Lambrev, Z. Liu, H.-S. Tan, C. S. Lo, S. Tretiak, S. Fernandez-Alberti\*, and Y. Zhao\*, *Sci. Rep.* 5, 13625 (2015).
- [3] “Photoinduced intra- and intermolecular energy transfer in Chlorophyll a Dimer”, F. Zheng, S. Fernandez-Alberti\*, S. Tretiak, and Y. Zhao\*, *J. Phys. Chem. B*, 121 (21), 5331–5339 (2017)
- [4] “Internal Conversion and Vibrational Energy Redistribution in Chlorophyll A”, P. M. Shenai, S. Fernandez-Alberti\*, W. P. Bricker, S. Tretiak, and Y. Zhao\*, *J. Phys. Chem. B* 120(1), 49-58 (2016).