# Modeling of Molecular Excitation Relaxation in Thermal Environment by Time-dependent Variational Approach with Superposition of Davydov D2 Ansätze

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Theoretical description of molecular excitation dynamics is a complex quantum mechanical problem, because interactions between all constituent parts of a molecule have to be considered at an ab-initio level. Therefore, complex quantum chemistry methods exist, which are capable of computing molecular excited state energy levels, transition dipole moments, vibrational mode frequencies, oscillation strengths and other microscopic molecule properties.

A problem of excitation energy relaxation involves degrees of freedom (DOF) beyond an isolated molecule, thermal fluctuations of molecule environment must be also treated. These are essential for thermodynamically correct excitation energy relaxation modeling. Due to e.g. internal-conversion (IC), a big portion of excitation energy is quickly transformed into molecular vibrational energy (heat), which ought to redistribute among all vibrational degrees of freedom, including those of environment, and, eventually, thermodynamic equilibrium should be restored. Thermal energy redistribution (TER) processes are important in both natural complexes and artificial structures, but due to a large number of interacting DOFs, modeling becomes a challenge. It has been recently demonstrated that this approximation is not accurate for carotenoids and TER processes have to be considered simultaneously [1].

We have created a general purpose molecular IC model where molecular DOFs are treated exactly, while states of environment vibrational DOFs are represented by a superposition of Davydov D2 Ansätze (sD2). A set of equations was derived to calculate the model time evolution. Also, algorithms for considering environment DOFs at a finite temperature and their thermalization, when using sD2 wavefunction, were proposed. To validate algorithms, we have considered a model system and have shown that they are capable of representing environment DOFs at a finite temperature and are able to maintain their temperature, even when environment is under the influence of a molecule.

We have also performed simulations of β-carotene S2→S1 IC with simultaneous TER processes, using the constructed IC model, and have found that β-carotene IC occurs faster, when β-carotene nearest environment temperature increases.

## REFERNCES

[1] V. Balevičius Jr, T. Wei, D. Di Tommaso, D. Abramavicius, J. Hauer, T. Polívka, C.D.P. Duffy, The full dynamics of energy relaxation in large organic molecules: from photo-excitation to solvent heating, Chem. Sci. **10** (18), 4792–4804 (2019).