Theory of Photoinduced Excited State Proton Transfer

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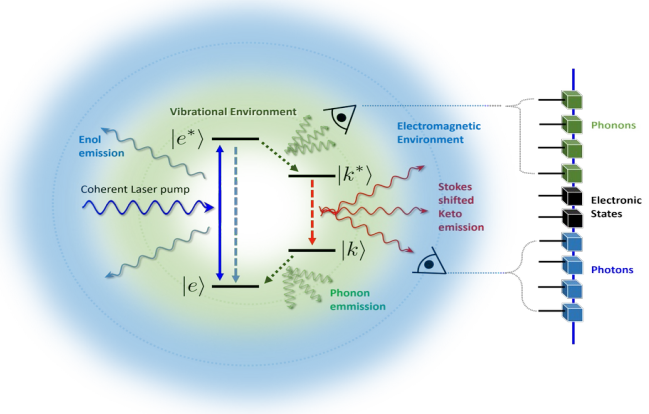

Scheme of intramolecular ESPT between an enol and a keto form. The Tensor-Network formalism allows to study the exchanges between the electronic main system and the surrounding environments [1].

Photoinduced Excited State Proton Transfer (ESPT) is characterized by a transfer of a proton between two moieties of a molecule when the system is photoexcited, often seen via an exceptionally large (≥ 8000 cm^{-1}) Stokes shift in fluorescence spectra. The efficiency of photoinduced ESPT reactions is critical for the light reactions of photosynthesis and light-driven enzyme biosynthesis [2]. Remarkably, EPST can be a truly ultrafast process that occurs on timescales at the limit of many experimental probes - just a few tens of femtoseconds. However, the theoretical understanding of ESPT at such very short timescales - and where quantum dynamical effects are likely to be important - still needs to be developed, and could open up novel opportunities for new light-harvesting applications. By developing simple prototype systems, we focused especially on short time behaviors parametrized by the photoexcitation shape and vibrations of the system. This surrounding environment is included with great accuracy through fully quantized theoretical simulation and powerful numerical Tensor-Network techniques [3], permitting us to include hundreds of vibrations modes. Studying the wavepacket propagation of test bed molecule models for ultrafast ESPT with explicit description of vibrations, we revealed the importance of the pump duration on initial conditions and on the subsequent dynamics. The presented study helps gain insight into the non-equilibrium dynamics of proton transfer and provides new design principles mimicking this natural and essential process.

References

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