

Ultrafast dynamics and spectroscopy of molecules coupled to a cavity mode

Oriol Vendrell*, Johana A. Gomez, and Inga S. Ulusoy

*Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg
Im Neuenheimer Feld 229, 69120 Heidelberg, Germany*

*oriol.vendrell@pci.uni-heidelberg.de

In this talk we address recent theoretical advances on the possibility to steer and influence the dynamics of photo-triggered chemical reactions of single molecules and molecular ensembles coupled to quantized light modes [1, 2].

From a theoretical perspective, the quantum dynamics of the molecular degrees of freedom (vibrational and electronic) and light modes is described consistently within the time-dependent Schrödinger equation using the highly efficient multi-configuration time-dependent Hartree (MCTDH) approach [3, 4].

Our simulations show that the dynamics unfolding immediately after photo-excitation strongly depend on whether the upper or lower polaritonic states are populated by the laser pulse [1], and on the life-time of the quantized mode. Whereas excitation of the lower polaritonic state leads to dynamics resembling the time-evolution of the uncoupled systems, excitation into the upper polaritonic states introduces a time-delay to the photo-triggered process, which is caused by the decay time through the manifold of dark states in the system [2]. As a representative example, we consider a poly-atomic organic molecule (pyrazine) featuring an ultrafast internal conversion channel from the S_2 to the S_1 electronic state, for which we show how strong light-matter coupling slows down this channel and can even completely close it [1].

References

- [1] I.S. Ulusoy, J.A. Gomez, O. Vendrell, *J. Phys. Chem. A* **123**, (2019), 8832
- [2] O. Vendrell, *Phys. Rev. Lett.* **121** (2018) 253001
- [3] O. Vendrell, *Chem. Phys.* **509** (2018) 55
- [4] H.-D. Meyer, U. Manthe, L.S. Cederbaum, *Chem. Phys. Lett.* **165** (1990), 73