Three-pulse photon echo spectra at conical intersections: model dissipative quantum dynamical studies

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Three-pulse photon echo signals for two model systems exhibiting strong vibronic interactions mediated by conical intersections are simulated using the equation-of-motion phase-matching approach combined with a dissipative treatment of the quantum dynamics.

In recent years, intensive research efforts have been devoted to the understanding of the effects of coherent vibrational motion and vibronic interactions in time-resolved electronic spectroscopy.
In particular, a number of experimental and theoretical studies have been devoted to the specific signatures of conical intersections on the spectra.

Among the variety of existing experimental techniques, three-pulse photon echo spectroscopy (3PPES) has become popular and the implementation of 3PPES in the UV domain has opened the door to the study of the excited state dynamics of important molecular chomophores.
Because these systems are more amenable to ab-initio modeling, it is hopped that a better understanding of the effect of vibronic couplings on multidimensional electronic spectra can be obtained. However, even for relatively small molecular systems, the computation of multidimensional spectra remains a computationally demanding task and one has to rely on relatively simple models.

In this contribution, we simulate 3PPE spectra for two different models involving conical intersections (CIs). The first model is a well established two-dimensional model of pyrazine describing the ultrafast decay of the initially excited ππ* state to the lower nπ* state through an accessible CI. We complement earlier studies on this model [1] by incorporating the effect of dissipation in our calculations.

The second model is a two-dimensional model describing the coherent motion on the lowest optically accessible excited state of pentafluorobenzene, caused by a strong ππ*-πσ* interaction and the resulting higher-lying CI. Time-resolved pump-probe [2] and photoelectron [3] spectra of this molecule have revealed long-lived oscillations. In this work, we analyze the signature of this specific coherent vibronic motion in 3PPE spectra.

Calculations are performed with the equation-of-motion phase matching approach and the dissipation is treated in the framework of the multi-level Redfield theory.
The specific signatures of the two different types of CIs in 2D PE signals and in the resulting beating maps are analyzed.

[1] J. Krčmář, M. Gelin, D. Egorova, W. Domcke, *Signatures of conical intersections in two-dimensional electronic spectra* , J. Phys. B **47,** 124019 (2014).
[2] S. A. Kovalenko, A. L. Dobryakov, and V. Farztdinov, *Detecting Electronic Coherence in Excited-State Electron Transfer in Fluorinated Benzenes*, Phys. Rev. Lett. **96**, 068301 (2006).
[3] O. Hueter et al, JCP, *submitted*