Transient Absorption 2D Correlation Spectroscopy – A Kinetic Model Free Approach to the Analysis of Ultrafast Spectroscopy Data

Julian Hniopek[1,2], Carolin Müller[1,2], Thomas Bocklitz[1,2], Michael Schmitt[2], Benjamin Dietzek[1,2], Jürgen Popp[1,2]

julian.hniopek@uni-jena.de

1: Leibniz Institute of Photonic Technology, Jena, Germany

2: Institute of Physical Chemistry & Abbe Center of Photonics, Friedrich Schiller University, Jena ,Germany

Abstract

Time-resolved femtosecond transient absorption (fs-TA) spectroscopy is a powerful method to investigate the photoinduced processes in molecular systems, that is, their relaxation and reaction pathways upon photoexcitation on time scales between a few femtoseconds and hundreds of nanoseconds. Analysis of the resulting set of spectra generally requires advanced techniques which try to fit a kinetic model to the data, for example *via* global lifetime analysis or multivariate curve resolution. While these methods are widely used, they require *a priori* information on the sampled system, as they require a kinetic model, i.e., the number of processes contributing to the data. Choosing the right number of processes is often not an easy task and heavily influences the results.[1]

2D correlation spectroscopy (2DCOS), a method popular especially in the field of vibrational spectroscopy, offers a way to analyze systematic changes in datasets recorded under a changing external variable, by recovering the cross-correlation function of the spectral variables.[2] 2DCOS is ideally suited to TA spectroscopy, as the external variable (time) is inherent to the method. Furthermore, it does not require a specific kinetic model or other *a priori* information. TA-2DCOS allows the extraction of the number of kinetic processes contributing to the data set alongside qualitative spectral signatures. We demonstrate that TA-2DCOS can reproduce the results obtained by common, model dependent, methods for well understood systems. 2DCOS can therefore serve as an alternative analysis method for fs-TA spectra and offer an ideal starting point for quantitative methods, if *a priori* information is not available.[3]

Acknowledgement: This work was supported by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) in the framework of SFB/TRR 234 CataLight (subprojects C2 and A1, project number 364549901) and project BO 4700/4-1..

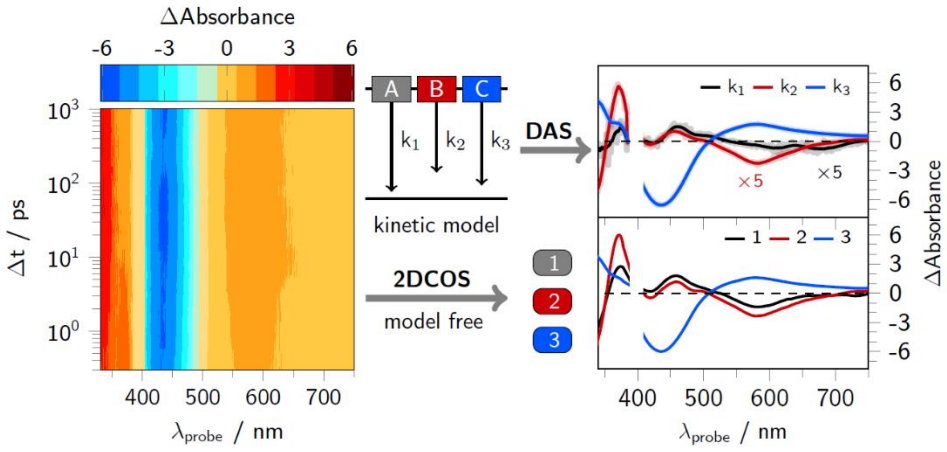

Figure 1: Contour plot of a fs-TA data set (left) with the results obtained by global lifetime analysis (right, top) and TA-2DCOS (right, bottom). The results of both methods agree very well, showing the validity of the 2DCOS approach.

[1] T. Cheshire et al., *J. Phys. Chem. B*, **124** (2020), 5971-5985

[2] I. Noda et al., *Appl. Spectrosc.*, **54** (2000), 236A-248A

[3] J. Hniopek et al., *J. Phys. Chem. Lett.*, **12** (2021), 4148-4153