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2020

Do, T. N., Sim J. H. N., Nguyen H. L., Lu, Y., Tan, H.-S. (2020). Application of two-dimensional optical spectroscopy: from ultrafast spectral diffusion to Lewis basicity. Proc. Of the 7th Asian Spectroscopy Conference (ASC 2020). doi:10.32655/ASC_8-10_Dec2020.48

<https://hdl.handle.net/10356/144303>

https://doi.org/10.32655/ASC_8-10_Dec2020.48

Application of two-dimensional optical spectroscopy: From ultrafast spectral diffusion to Lewis basicity

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Abstract

Two-dimensional optical spectroscopy (2DOS) is the optical version of the well-established 2D-NMR technique, e.g., COSY. With time resolution in the femtosecond regime, 2DOS is widely used to resolve the ultrafast frequency modulation dynamics, such as spectral diffusion, in various vibrational [1-2] and electronic [3-4] systems.

Chlorophylls (Chls) *a* and *b* are two main types of photosynthetic pigments responsible for the light-harvesting and energy regulation of green plants on Earth. Here, we employ 2DOS to track the time evolution of the 2D peakshape (Fig. 1) and resolve the ultrafast spectral diffusion dynamics of the Chl Q_y transition in various organic solvents. The obtained results suggest that Chls exhibit three different relaxation dynamics with the timescales of sub-picosecond (sub-ps), several ps and tens to hundreds of ps. The correlation between spectral diffusion timescales and the solvents' Lewis basicity, together with the support of *ab initio* time-dependent density functional theory (TDDFT) calculations indicates that we are probing directly the fluctuation dynamics of the dative bond between the solvent's lone pair and the electrophilic Mg^{2+} center of Chls. This dative bond is responsible for the solvent Lewis basicity. 2DOS therefore enables a time-resolved molecular level observation corresponding to an important macroscopic chemical property – Lewis basicity.

Fig. 1: Representative 2D spectra of Chl *a* dissolved in THF (top) and pyridine (bottom).

Keywords: 2D spectroscopy, ultrafast, spectral diffusion, Chlorophyll.

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