Mixed IR/VIS Multidimensional Spectroscopies: Chemistry and Biophysics in Realtime

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Multidimensional experiments, daily business in the field of NMR, have been demonstrated only relatively recently in IR spectroscopy [1]. Similar as nuclear spins in multidimensional NMR, molecular vibrations are employed in multidimensional IR as probes of molecular structure and dynamics, albeit with femtosecond time resolution.

Our use of mixed IR/VIS pulse sequences considerably extends the potential of multidimensional IR spectroscopy, enabling studies of ultrafast nonequilibrium processes as well as surface specific, highly sensitive experiments. A UV/VIS pulse preceding the IR pulse sequence can be used to prepare the system under study in a nonequilibrium state. 2D-IR snapshots of the evolving nonequilibrium system can be taken to monitor structural changes, for example during a light triggered reaction or during the photocycle of a light sensitive protein. Transfering the system to a nonequilibrium state by electronic excitation during the IR pulse sequence allows for correlating states of reactant and product of the light triggered process via their 2D-IR cross peaks – a nonequilibrium 2D-IR version of exchange spectroscopy. Introduction of a non-resonant VIS pulse at the end of the IR part of the experiment selectively upconverts the infrared signal of interfacial molecules to the visible spectral range by sum frequency generation, enabling femtosecond surface 2D-IR spectroscopy with submonolayer sensitivity [2].

[1] W. Zhuang, T. Hayashi and S. Mukamel, *Angew. Chem. Int. Ed.* **48**, 3750 (2008).

[2] J. Bredenbeck, A. Ghosh, H.-K. Nienhuys and M. Bonn, *Acc. Chem. Res.* **42**, 1332 (2009).