

IL 6: 2D-IR spectroscopy: chemistry and biophysics in real time

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Pulsed multidimensional experiments, daily business in the field of NMR spectroscopy, have been demonstrated only relatively recently in IR spectroscopy. Similar as nuclear spins in multidimensional NMR, molecular vibrations are employed in multidimensional IR experiments as probes of molecular structure and dynamics, albeit with femtosecond time resolution. Different types of multidimensional IR experiments have been implemented, resembling basic NMR experiments such as NOESY, COSY and EXSY. In contrast to one-dimensional linear spectroscopy, such multidimensional experiments reveal couplings and correlations of vibrations, which are closely linked to molecular structure and its change in time [1].

The use of mixed IR/VIS pulse sequences further 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 are then taken, for example during a photochemical reaction or during the photocycle of a light sensitive protein [2]. Preparing the system in a nonequilibrium state by UV/Vis 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 technique that has been used to map the connectivity between different binding sites of a ligand as it migrates through a protein [3]. Introduction of a non-resonant VIS pulse at the end of the IR part of the experiment allows to selectively upconvert the infrared signal of interfacial molecules to the visible spectral range by sum frequency generation. In this way, femtosecond interfacial 2D-IR spectroscopy can be implemented, achieving submonolayer sensitivity [4].

[1] W. Zhuang, T. Hayashi and S. Mukamel, *Angew. Chem. Int. Ed.* **48**, 3750-3781 (2008), Z. Ganim, H. S. Chung, A. W. Smith, L. P. Deflores, K. C. Jones, A. Tokmakoff, *Acc. Chem. Res.* **41**, 432-441 (2008), R. M. Hochstrasser, *Proc. Natl. Acad. Sci.* **104**, 14190 (2007), a selection of reviews can be found in the following special issue *Acc. Chem. Res.* **42**, 9, 1207-1469 (2009).

[2] J. Bredenbeck, J. Helbing, C. Kolano and P. Hamm, *ChemPhysChem.* **8**, 1747-1756 (2007); P. Hamm, J. Helbing and J. Bredenbeck, *Annu. Rev. Phys. Chem.* **59**, 291-317 (2008).

[3] J. Bredenbeck, J. Helbing, K. Nienhaus, G. U. Nienhaus and P. Hamm, *Proc. Natl. Acad. Sci.* **104**, 14243-14248 (2007).

[4] J. Bredenbeck, A. Ghosh, H.-K. Nienhuys and M. Bonn, *Acc. Chem. Res.* **42**, 1332-1342 (2009).