

Rapid-Scan 2D Fluorescence Spectroscopy

Simon Draeger*, Sebastian Roeding, Andreas Steinbacher, Jakub Dostál, Tobias Brixner

Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany, *simon.draeger@phys-chemie.uni-wuerzburg.de

We implement liquid-phase 2D spectroscopy with collinear four-pulse excitation and fluorescence detection. Pulse-sequence parameters are varied on a shot-to-shot basis using a fast pulse shaper. A complete set of all third-order signals (photon echo, double-quantum coherence, etc.) is acquired via 27-fold phase cycling in just 6 s plus averaging.

We present a novel all-collinear setup to perform pulse-shaper-assisted 2D electronic spectroscopy with fluorescence detection in the liquid phase (Fig. 1a). Phase cycling [1] is used to extract the desired coherent information from the incoherent fluorescence signal.

Fluorescence 2D spectroscopy has been demonstrated in the literature previously [2, 3]. In our implementation we employ a fast pulse shaper (Dazzler, Fastlite) allowing us to vary the interpulse time delays and relative phases on a shot-to-shot basis. Thus we realize rapid scanning and 27-fold phase cycling. This allows us to retrieve all third-order contributions simultaneously, out of which the desired linear combinations (rephasing and non-rephasing photon echo, double-quantum coherence, reverse transient grating, etc.) can be constructed. Mechanical translation stages are not required, i.e. the setup is inherently phase stable. In the example shown here, we acquire 15 coherence time steps in both directions, thus requiring a total of $15 \times 15 \times 27 = 6075$ pulse shapes for each population time. At 1 kHz repetition rate, a full 2D spectrum is obtained in 6 s measurement time. Additional intervals can be used for averaging or other population times.

We exemplify the technique on cresyl violet in ethanol and acquire 31 population time steps (in ~ 3 min without averaging). Data at $T = 100$ fs is shown in Fig. 1b (top) for 142-fold averaging. The results are compared with conventional noncollinear 2D spectroscopy (Fig. 1b, bottom). We observe a signal oscillation over population time (Fig. 1c), in agreement with literature [4], which is attributed to vibrational coherences in the excited state.

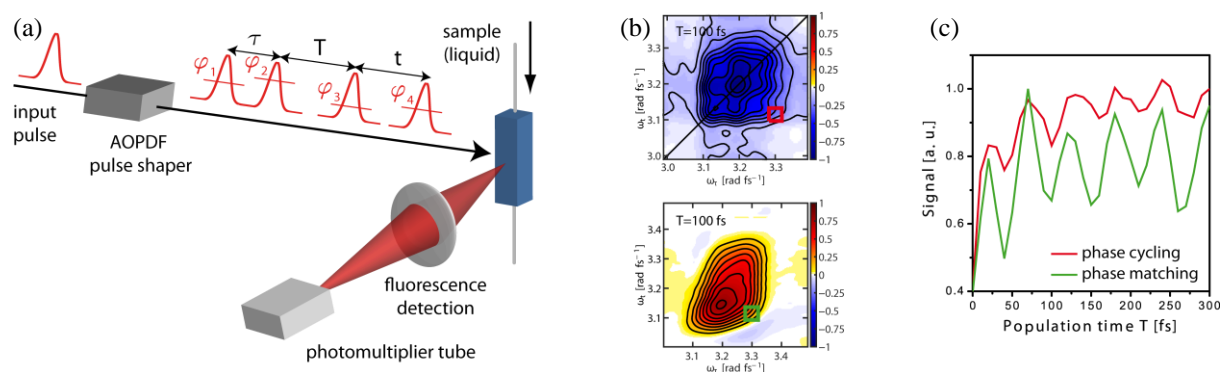


Fig. 1. (a) Experimental setup. The pulse sequence is varied on a shot-to-shot basis using an acousto-optic programmable dispersive filter (AOPDF). (b) Absorptive spectra in collinear fluorescence (top) and noncollinear geometry (bottom). The different signs result from different numbers of interactions with the ket side of the Feynman diagram. (c) Off-diagonal signals from regions marked in (b) as a function of population time in collinear (red) and noncollinear geometry (green) reveal an oscillatory behavior due to vibrational coherence.

- [1] H.-S. Tan, *J. Chem. Phys.* **129**, 124501 (2008)
- [2] P. Tian *et al.*, *Science* **300**, 1553 (2003)
- [3] P. F. Tekavec *et al.*, *J. Chem. Phys.* **127**, 214307 (2007)
- [4] D. Turner *et al.*, *J. Phys. Chem. Lett.* **2**, 1904 (2011)