Collinear two dimensional infrared spectroscopy with a phase-locked pulse pair delayed by a birefringent delay line

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Abstract: We perform two dimensional spectroscopy in the mid-IR by using a set of birefringent wedges to generate and delay a phase-locked pair of pump pulses.

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Two-dimensional (2D) spectroscopy in the partially collinear pump-probe geometry requires the generation of a pair of phase-locked collinear pump-pulses. We previously introduced the Translating-Wedge based Identical pulses eNcoding System (TWINS) as a simple and robust technique for the generation of phase-locked pulses with exceptional stability and demonstrated its applicability to 2D electronic spectroscopy (2DES) in the visible range [1]. This device exploits birefringent materials in which two orthogonal polarizations experience different group velocities, to create highly controlled delayed pulse replicas.
Here,we extend the TWINS concept to the mid-infrared spectral range and demonstrate its applicability to 2DIR spectroscopy. For a proof of concept we use as birefringent medium Lithium Niobate, which allows transmission of light up to 5μm. We introduced the TWINS device in the pump beam of a pump-probe experiment to perform 2D IR spectroscopy in the collinear geometry. The setup is illustrated in Fig.1.

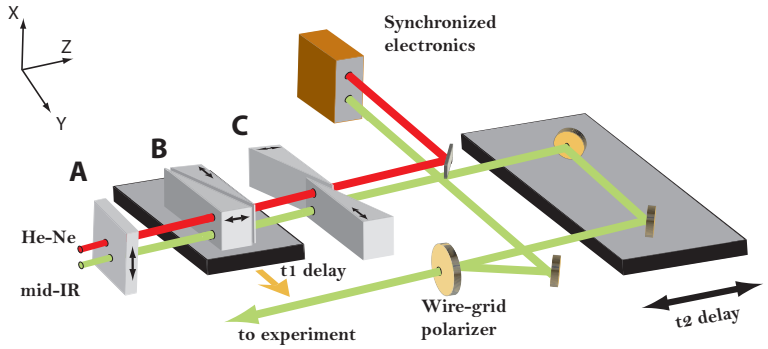

Fig. 1. Principle of the 2D experiments with TWINS device, which is constituted of blocks A, B and C. Arrows indicate the orientation of the optical axis in each elements.

A mid-IR beam is sent through the TWINS with 45° polarization, generating two collinear, equally intense and perpendicularly polarized pulses separated by a delay t_1, which depends on the insertion of the moving wedges (block B in Fig.1). A wire-grid polarizer can be used to project their polarization to a common direction. The reflection from this polarizer is used to monitor the interference between the two pump pulses and to phase correctly the 2D spectra. An additional He-Ne beam is used to monitor the position of the moving pair of wedges synchronously with the mid-IR laser pulses. This allows first, to bin and average the data from different scans, and second, to scan continuously the wedges while acquiring data. This permits to achieve fast recording of a 2D spectrum [2].

To test the apparatus, we performed 2D IR measurements on a sample of 5% of HOD in H_2O. A sequence of 2D maps recorded for different values of the population time t_2 is shown in Figure 2. The OD stretch vibration gives rise to an intense and inhomogeneously broadened absorption band around 2500 cm^{-1}. We observe a positive signal due to the 0-1 transition (bleach and stimulated emission, blue) and a negative signal due to the 1-2 transition (transient absorption, red). The tilt of the 2D-IR signal as a function of delay between pump-pulses and probe is a measure of the correlation between pump and probe vibrational frequencies. This correlation is lost on a picosecond timescale, and this dynamics is related to the fluctuations of the hydrogen bond network of water, as previously reported.

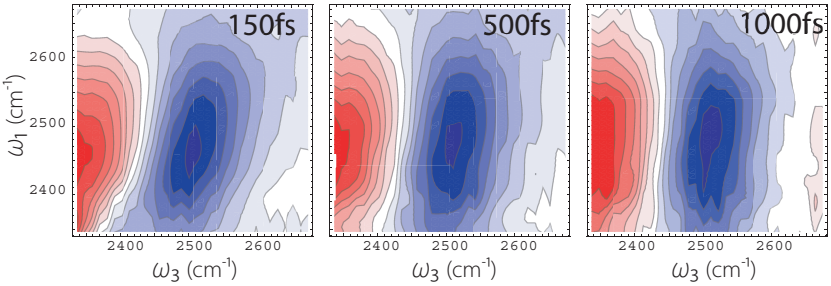

Fig. 2. 2D-IR spectra of HOD in H_2O, with the XXXX polarization condition, at different population times indicated in the upper right corner.

On Figure 3 are displayed some example spectra with the XYXY polarization. This configuration requires to remove the polarizer in the pump and to place one in the probe beam after sample. The probe beam at the sample could be made approximately 10 times stronger than in the experiment with all parallel polarizations shown in Fig. 2. As a result, the signal to noise ratio at short waiting times is much better. Since only the anisotropic signal is amplified, isotropic background due to heat is suppressed [3]. However, the signal decays very quickly with the loss of anisotropy due to fast reorientation (less than 1 ps) of the O-D transition dipole.

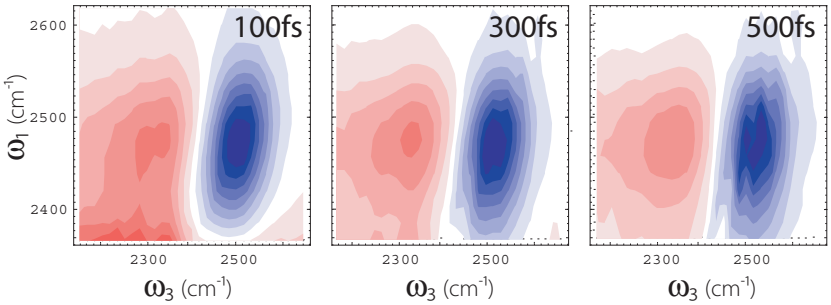

Fig. 3. 2D-IR spectra of HOD in H_2O, with the XYXY polarization condition, at different population times indicated in the upper right corner.

In conclusion, we present a new technique to perform collinear 2D-IR spectroscopy. It is simple and reliable, and can be easily implemented in a standard pump-probe experiment. In future work, we plan to extend its application to the full mid-IR range with other materials such as Hg2Cl2 (Calomel) which displays very large birefringence and transparency up to 20 μm.

References

1. D. Brida, C. Manzoni, and G. Cerullo, "Phase-locked pulses for two-dimensional spectroscopy by a birefringent delay line," Opt. Lett. **37**, 3027–3029 (2012).
2. J. Helbing and P. Hamm, "Compact implementation of fourier transform two-dimensional IR spectroscopy without phase ambiguity," J. Opt. Soc. Am. B **28**, 171–178 (2011).
3. J. Réhault and J. Helbing, "Angle determination and scattering suppression in polarization-enhanced two-dimensional infrared spectroscopy in the pump-probe geometry," Opt. Express **20**, 21,665–21,677 (2012).