Time-resolved spectroscopy with two frequency-stabilized mode-locked lasers

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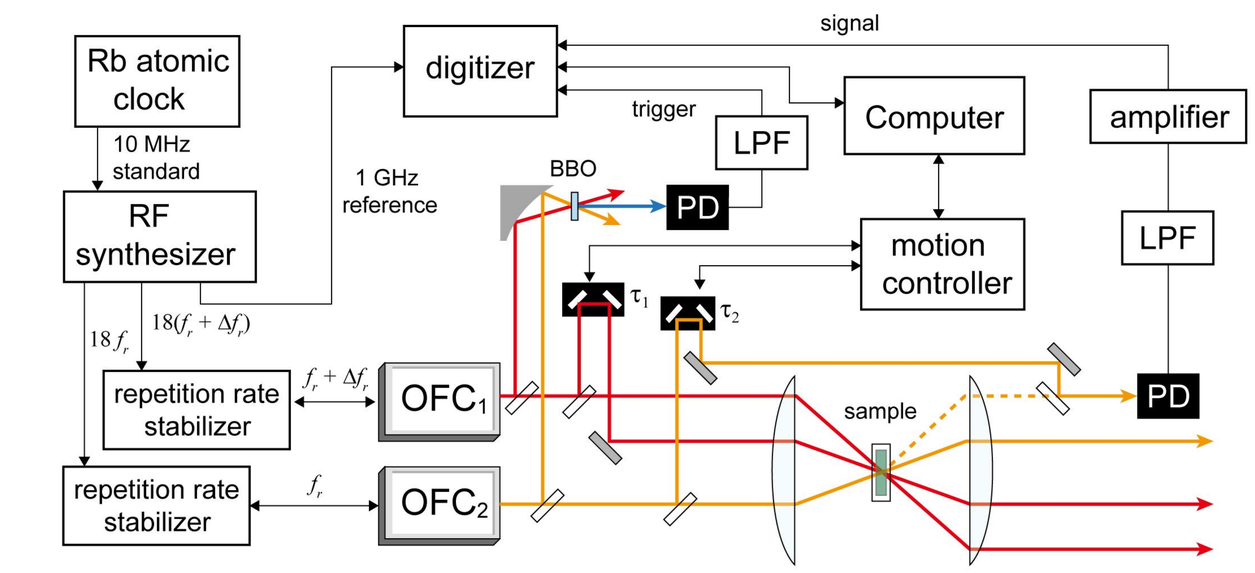
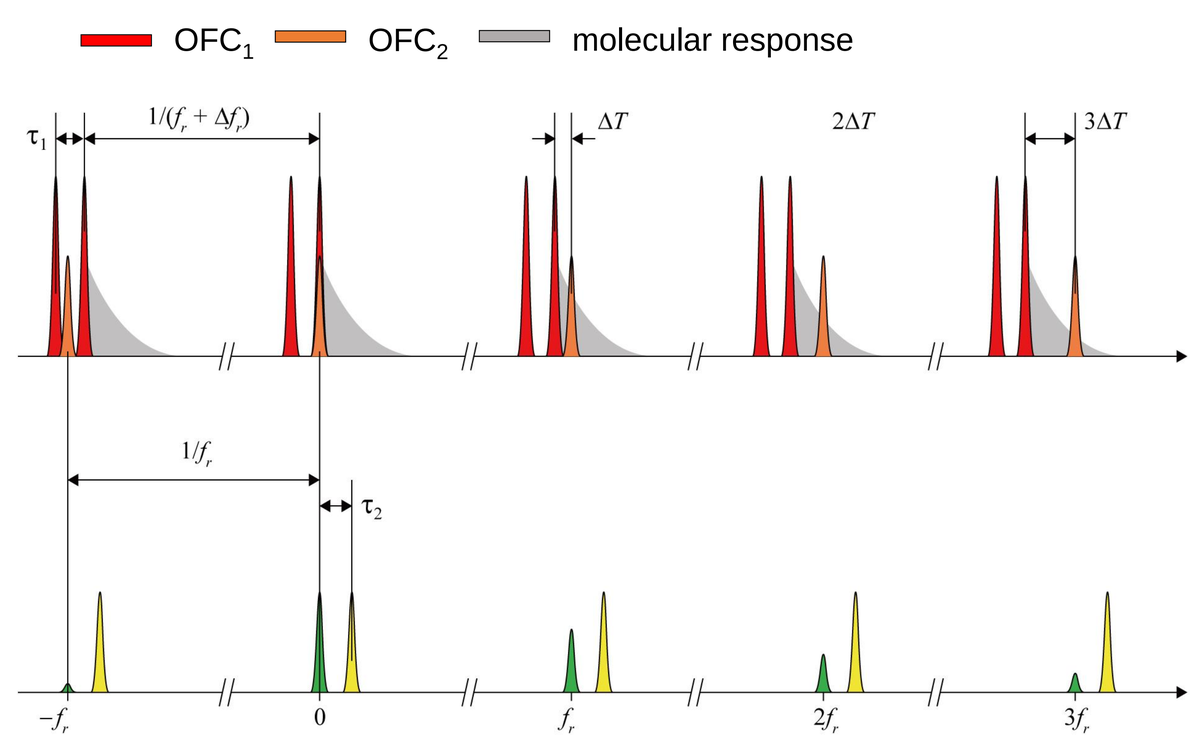
Femtosecond laser has brought a dramatic development on time-resolved spectroscopy to understand the complex photochemical reactions in nature. In time-resolved spectroscopy, an impulsive pump pulse generates a non-equilibrium state, and its time evolution is monitored by a probe pulse. The time delay between the pump and probe is generated by adjusting the optical path-length difference between the two pulses conventionally. Because the experiments with mechanical time-delay have to record the data at a fixed time-delay, they require high time costs to observe slow reaction dynamics and to obtain a high resolution time-domain vibrational spectrum.

Recently, we have demonstrated dual frequency-comb (DFC) based time-resolved spectroscopy. [1-2] Frequency comb being a special type of mode-locked laser has equally spaced spectral lines fixed at the frequencies specified by the laser repetition frequency and a offset frequency. When the repetition rates of two frequency combs are slightly detuned, the time-delay between them are automatically generated. The time-delay generated by DFC does not change the phase-front of the delayed beam, so that it enables wave mixing experiments such as transient absorption and two-dimensional spectroscopy even at nanosecond time delay. The use of single-point photodetector and intrinsically fast time-delay scan rate are also unique properties of DFC spectroscopy. Here, we present three DFC-based time-resolved spectroscopy, and derived them theoretically based on frequency-comb field-adapted perturbation theory. [3]

Dual frequency-comb two-dimensional electronic spectroscopy (DFC-2DES)



RF: radio frequency, OFC : optical frequency comb, PD: photodetector, LPF: low-pass filter, BBO: beta-barium borate crystal

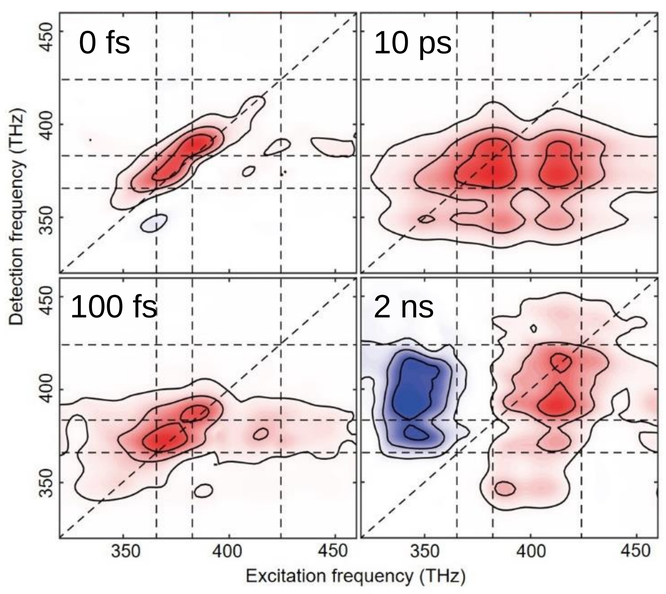


Exhaustive 2DES with analytical phase correction

Conventional 2DES numerically correct the phase of 2DES data by comparing it to a pump-probe data. On the other hand, analytical phase-correction and amplitude normalization are possible in DFC-2DES with an interferometric pump-probe spectrum, which can be measured at the same instrument.

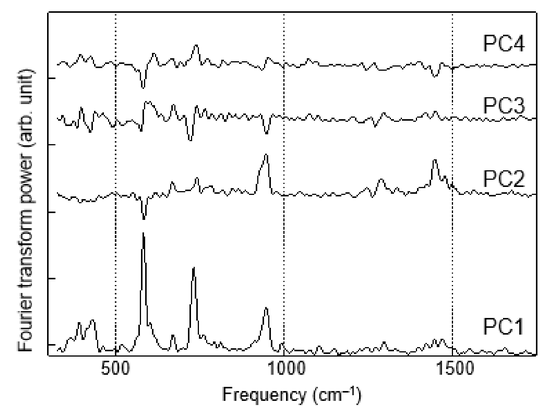
$$\exp\left[i\Phi_{TA}(\omega_2,T)\right]-1=\frac{\beta_2(\omega_2)E_{2D}(\omega_2,T)}{\alpha_1(\omega_2)E_1(\omega_2)}\equiv F(\omega_2)E_{2D}(\omega_2,T)$$

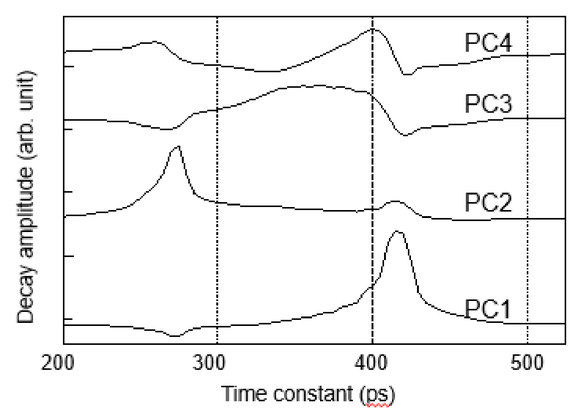
$$\text{with}\quad E_{2D}(\omega_2,T)\equiv\int d\omega_1 E_{2D}(\omega_2,T,\omega_1)$$

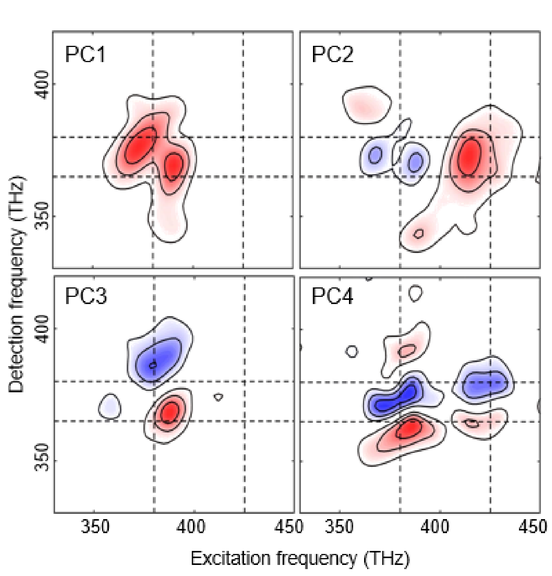


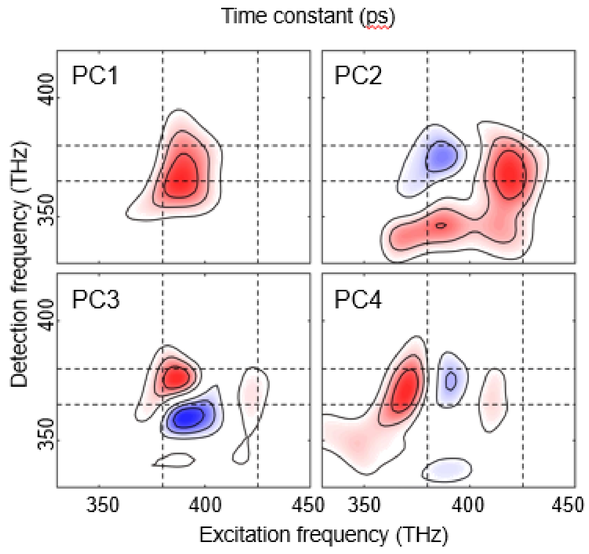
DFC-2DES is advantageous to observe coherent vibrational or electronic coherence with high frequency resolution and nanosecond electronic relaxation or photochemical reaction kinetics. Because (1) DFC-2DES does not consume additional data acquisition time for long T-scan. (2) The automatic T-scan of DFC conserves the spatial beam quality of the delayed beam during long T-scan,

Principal component analysis on DFC-2DES data









Conclusion

As a matter of proof, we measured the DFC-2DES data of IR125 ethanol solution. The measured DFC-2DES data well represents from the time-evolution of the photo-induced population, coherent vibrational spectrum in excitation-frequency-resolved manner. A careful data analysis of DFC-2DES can deduce the correlation between the electronic structure and molecular structure of a complex photochemical reaction system.

[1] *J. Phys. Chem. Lett.*, **9**, 1866-1871 (2018)
[2] *J. Phys. Chem. B*, **122**, 9775-9785 (2018)
[3] *Chem. Phys.*, **522**, 120-137 (2019)