Frequency-comb for physical chemistry: Dual-comb linear and nonlinear spectroscopy in condensed phase

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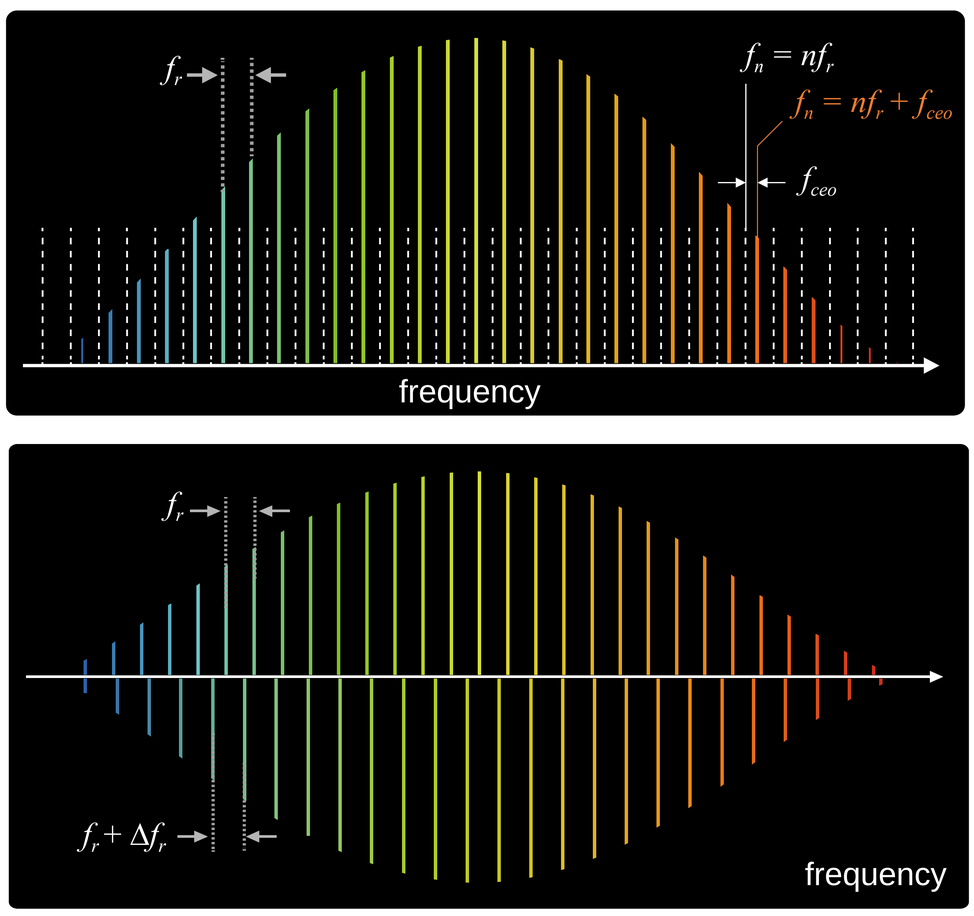
The spectrum of multi-mode laser is has a comb-like structure. The frequency of *n*-th comb tooth of the laser can be expressed as $f_n = n f_r + f_{ceo}$, where f_r is the repetition rate, which is determined by the laser cavity length, and f_{ceo} is called the carrier-envelope-offset frequency, which arise from the mismatch between phase velocity and group velocity in the laser cavity. When both f_r and f_{ceo} of a laser are stabilized, the laser is called frequency comb. Based on RF frequency locking techniques, frequency comb has been widely used in physics for precision measurement and gas-phase spectroscopy. In condensed phase, the molecular electronic transition lines is broad as much as tens of THz due to its inhomogeneity and fast relaxation processes. Therefore, the high frequency resolution of frequency comb has not been necessary for condensed phase spectroscopy.

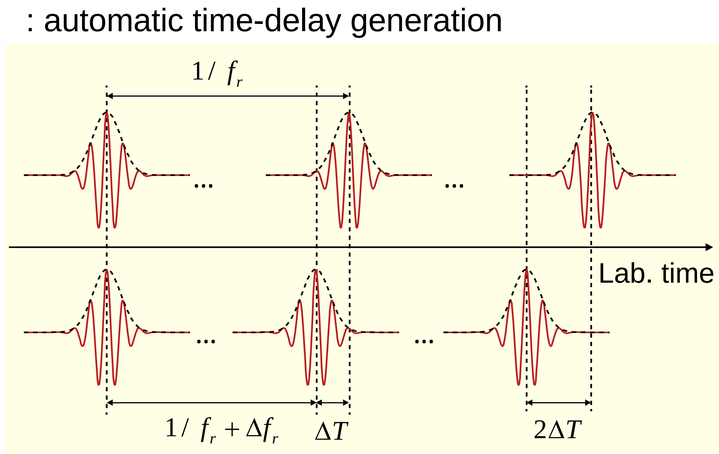
Dual frequency-cob (DFC) is the key to combine the frequency comb and conventional spectroscopy for chemistry. DFC utilizes two independent optical frequency-combs (OFC) with slightly detuned repetition rates. We have proposed DFC absorption spectroscopy [1] and DFC transient absorption [2] with a broadband-Ti:sapphire-laser based DFC system, which enabled us to resolve broad electronic transition character and ultrafast dynamics of molecular systems in condensed phase. The unique properties of DFC, such as fast time-delay scanning, pulse-to-pulse phase-coherence and simultaneous multi-channel data recording, would enable us to measure unprecedented region of chemistry.

Dual frequency-comb (DFC)



Asynchronous optical sampling (ASOPS)

: automatic time-delay generation



By detuning the repetition rates of two independent frequency combs, a time-delay is generated with a increment ΔT

$$\Delta T = \frac{1}{f_r} - \frac{1}{f_r + \Delta f_r} \cong \frac{\Delta f_r}{f_r^2}$$

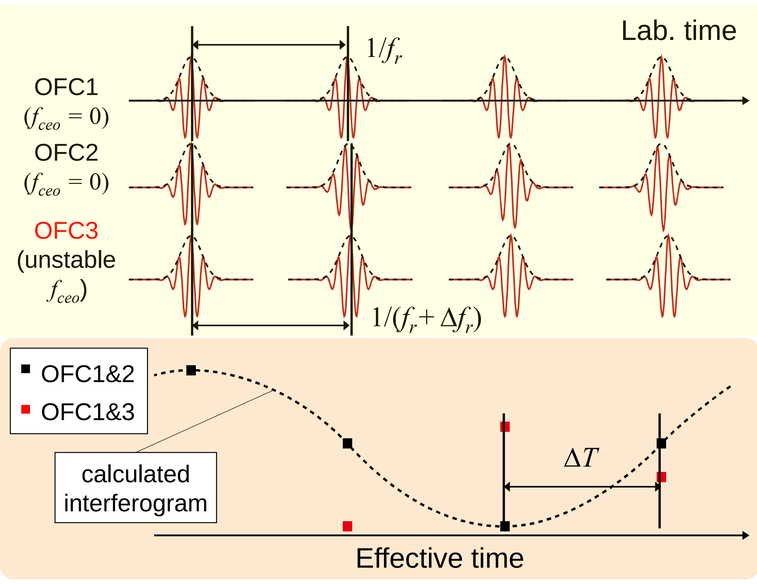
Then, the time delay between the pulses of the two OFCs, T, and the laboratory time, t, has a down conversion relation that

$$T = t\frac{\Delta f_r}{f_r}$$

Phase-coherence

The relation between carrier-envelope-phase, ϕ_{CE}, and f_{ceo}, shown in the right side determines how two electric field interfere.

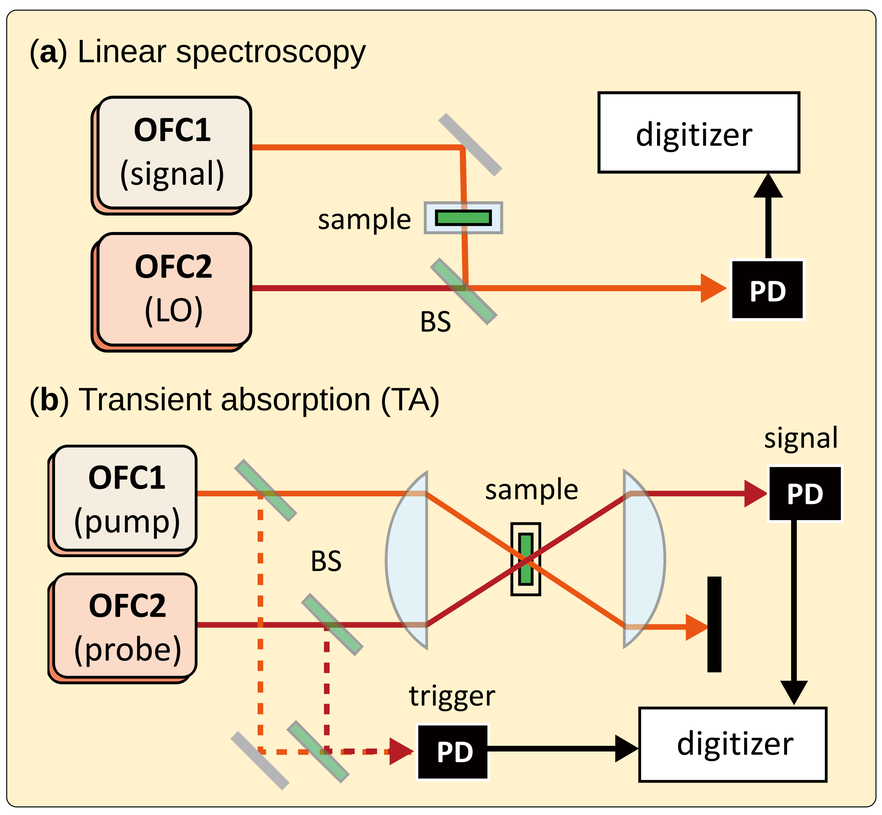
$$\phi_{CE} = 2\pi \frac{f_{ceo}}{f_r}$$



When $f_{ceo} = 0$, the optical interference in DFC system arises at a down-converted frequency f_{RF}

$$f_{RF} = f_{opt}\frac{\Delta f_r}{f_r}$$

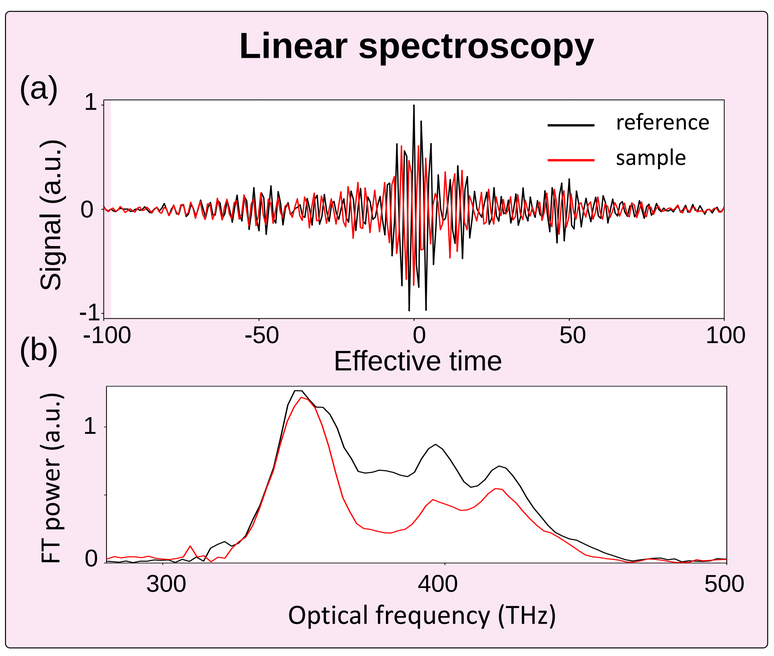
Experiment



The schematic diagram of DFC linear spectroscopy (a) and DFC-TA. f_r = 80 MHz, 80 MHz + Δf_r for OFC1 and OFC2, respectively. Every signal pass through a 48 MHz low-pass filter LO: local oscillator, PD: photodetector, BS: beam splitter.

Result

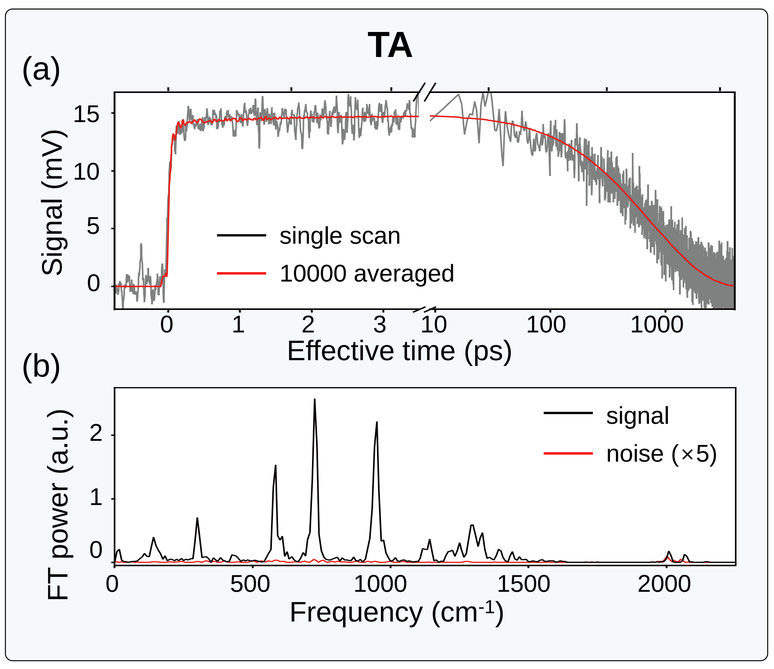
Linear spectroscopy



DFC spectroscopy

The interference pattern between the two OFCs changes when one of OFCs passes a sample, because of its response. (a) shows a single-scan DFC interferogram with and without the sample/ The real and imaginary part of the sample can be extracted by comparing the Fourier transform of the interferograms, which is shown in (b). Since DFC-based experiment uses a single photo-detector, it is advantageous for the experiments requiring a simultaneous multi-parameter recording.

TA



DFC-TA

The population time of a sample can be scanned by non-collinearly overlapping the two OFCs. (a) shows the DFC-TA data of IR125 ethanol solution. DFC-TA can observe the kinetic dynamics of a sample within **1 ms** by controlling Δf_r, with S/N shown in (a). Simultaneously, DFC-TA can also be employed for studying ultrafast reaction dynamics with its time-resolution of **12 fs**. The coherent vibrational spectrum shown in (b) confirms its time resolution. The fast scan rate and high time-resolution of DFC-TA would be applied for various unexplored chemical reactions.

[1] B. Cho, *et al., Phys. Rev. A* **2018**, 97, 033831
[2] JW. Kim, *et al., J. Phys. Chem. Lett.* **2018**, 9, 1866-1871