Dual Frequency-Comb Transient Absorption Measurment Covering a Broad Dynamic Range

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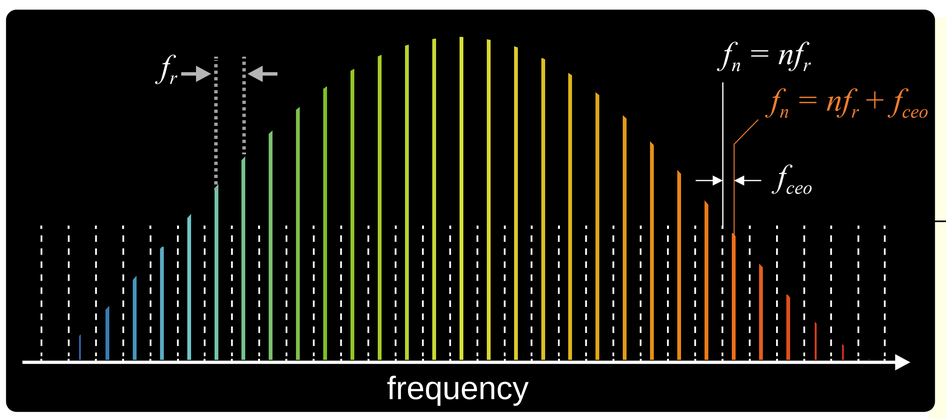
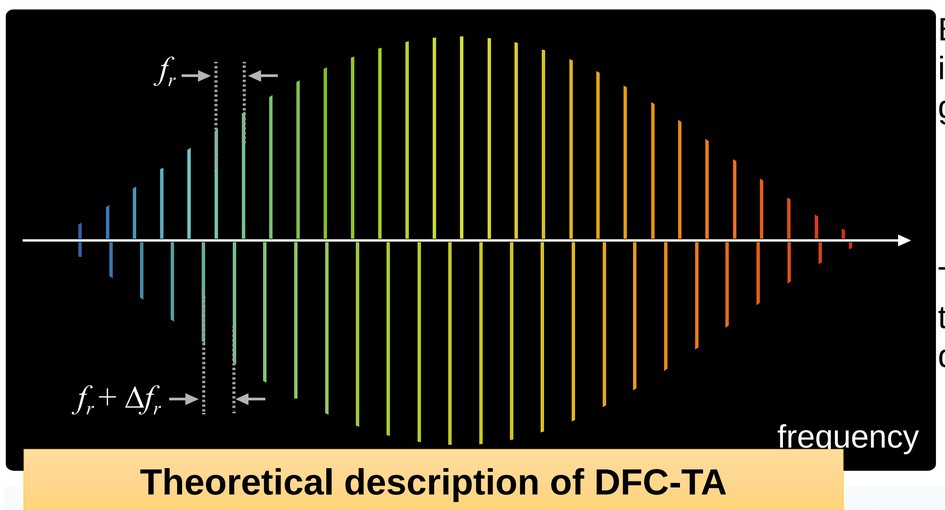
Optical frequency comb (OFC) has brought a remarkable advancement in gas-phase spectroscopy due to its high precision and accuracy. OFC is characterized by two parameters, i.e., repetition rate f_r and carrier-envelop-offset frequency f_{ceo}. In dual frequency comb (DFC) system with two phase-locked OFC lasers, the slightly detuned repetition rates of the two OFCs linearly changes the time delay between the pulses from different OFCs. Although DFC is a useful spectroscopic tool, DFC has not been actively employed for the studies of molecular reaction dynamics in condensed phases. The high frequency resolution of DFC cannot be brought out in condensed phases. The electronic coherence time of condensed phase, < 20 fs, is extremely shorter than that of gas phase, which is longer than tens of picosecond. In other words, most of pulses go to waste in condensed phase, because DFC has to scan as long as $1/f_r$, which is several nanoseconds. In addition, the broad electronic transition lines of molecules in condensed phases require a broadband light source. Recently, we demonstrated a dual-comb spectroscopy for molecules in condensed phase with a broadband Ti:sapphire laser based DFC.

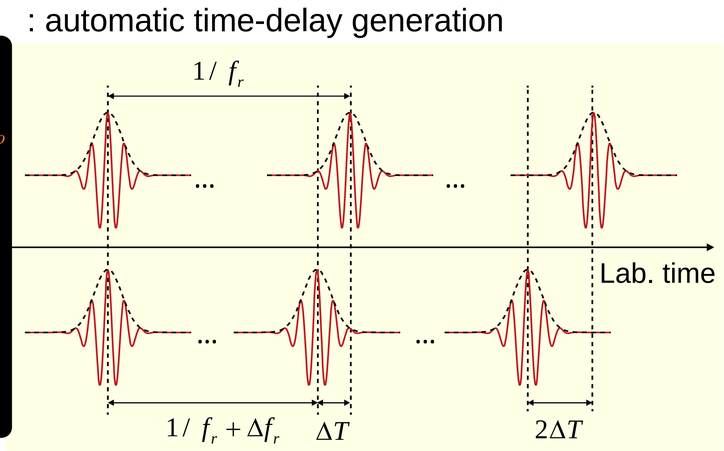
We here demonstrate a DFC-based transient absorption (DFC-TA) technique [1]. A notable difference between our DFC-TA and previous works is that our DFC-TA monitors the population dynamics of a system, whereas other workers measure the electronic coherence. Since many photochemical reactions of interest occur within tens of femtosecond (fs) to several ns, the full-scanning property of DFC without any mechanical delay stage is exceptionally useful. Further, the auto-scanning character of the DFC makes its experimental set-up much simpler than conventional mechanical scan-based TA techniques. In DFC-TA, once the pump and the probe beams are spatially overlapped at sample, we do not need to make pulses temporally overlapped, because two trains of pulses from dual comb lasers would cross during the data scan. In addition, the spatial beam quality of DFC-TA does not depend on the time delay between pump and probe pulses. Note that this aspect is usually critical in conventional TA experiments that require changing optical path length to scan the time delay.

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

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

Theoretical description of DFC-TA

OFC field: $E_j(\mathbf{r},t) = e^{i\mathbf{k}_j(\omega_{c,j})\cdot\mathbf{r} - i\omega_{c,j}t}\sum_{n=-\infty}^{\infty} A_{n,j}e^{-i2\pi n f_{r,j}t}$

carrier frequency: $\omega_c \equiv \omega_{c,1} = \omega_{c,2} - \Delta\omega_c$

repetition rate: $\omega_r \equiv \omega_{r,1} = \omega_{r,2} - \Delta\omega_r$

Third-order polarization density (two-level system)

$$P^{(3)}(\mathbf{k}_2,t) = \int_0^\infty dt_3\int_0^\infty dt_2\int_0^\infty dt_1$$
$$S_{RE}^{(3)}(t_3,t_2,t_1)\{E_2(\mathbf{r},t-t_3)E_1(\mathbf{r},t-t_3-t_2)E_1^*(\mathbf{r},t-t_3-t_2-t_1) + E_1(\mathbf{r},t-t_3)E_2(\mathbf{r},t-t_3-t_2)E_1^*(\mathbf{r},t-t_3-t_2-t_1)\}$$
$$+S_{NR}^{(3)}(t_3,t_2,t_1)\{E_2(\mathbf{r},t-t_3)E_1^*(\mathbf{r},t-t_3-t_2)E_1(\mathbf{r},t-t_3-t_2-t_1) + E_1(\mathbf{r},t-t_3)E_1^*(\mathbf{r},t-t_3-t_2)E_2(\mathbf{r},t-t_3-t_2-t_1)\}$$

Only two interaction pathways, which are rephasing (RE) and non-rephasing (NR), considered for simplicity.

[RE] $-k_A + k_B + k_C - k_s = 0$
[NR] $k_A - k_B + k_C - k_s = 0$

Inserting the OFC field into $P^{(3)}(\mathrm{k}_2,t)$

$$P^{(3)}(\mathbf{k}_2,t) = e^{i\mathbf{k}_2\cdot\mathbf{r}}\sum_{q,m,n=-\infty}^{\infty}\int_0^\infty dt_3\int_0^\infty dt_2\int_0^\infty dt_1$$
$$c_{q,m,n}^{RE}S_{RE}^{(3)}(t_3,t_2,t_1)\left\{e^{i\left[\left(\omega_{q,m,n}^{RE}-q\Delta\omega_r\right)(t_3-t)+\omega_{m,n}^{RE}t_2+\omega_n^{RE}t_1\right]} + e^{i\left[\left(\omega_{q,m,n}^{RE}-m\Delta\omega_r\right)(t_3-t)+\left(\omega_{m,n}^{RE}-m\Delta\omega_r+\Delta\omega_c\right)t_2+\omega_n^{RE}t_1\right]}\right\}$$
$$+c_{q,m,n}^{NR}S_{NR}^{(3)}(t_3,t_2,t_1)\left\{e^{i\left[\left(\omega_{q,m,n}^{NR}-q\Delta\omega_r\right)(t_3-t)+\omega_{m,n}^{NR}t_2+\omega_n^{NR}t_1\right]} + e^{i\left[\left(\omega_{q,m,n}^{NR}-n\Delta\omega_r\right)(t_3-t)+\left(\omega_{m,n}^{NR}-n\Delta\omega_r+\Delta\omega_c\right)t_2+\left(\omega_n^{NR}-n\Delta\omega_r+\Delta\omega_c\right)t_1\right]}\right\}$$

where the newly defined frequencies are

$$\omega_n^{RE} = -\omega_n^{NR} = -\omega_c - n\omega_r$$
$$\omega_{m,n}^{RE} = -\omega_{m,n}^{RE} = (m-n)\omega_r$$
$$\omega_{q,m,n}^{RE} = \omega_c + \Delta\omega_c + (q+m-n)\omega_r$$
$$\omega_{q,m,n}^{NR} = \omega_c + \Delta\omega_c + (q-m+n)\omega_r$$

The third-order susceptibility, $\tilde{S}^{(3)}\left(\omega_{q,m,n},\omega_{m,n},\omega_n\right)$, is obtained by conducting the triple integration on t_1, t_2 and t_3.

DFC-TA signal

Introducing one more OFC2 field as an LO.

$$S_{DFC-TS}(t,\tau) \propto 2\,\mathrm{Re}[E_2^*(\mathbf{k}_2,t-\tau)E^{(3)}(\mathbf{k}_2,t)]$$
$$\propto 2\,\mathrm{Im}[E_2^*(\mathbf{k}_2,t-\tau)P^{(3)}(\mathbf{k}_2,t)]$$
$$\propto \sum_{p,q,m,n=-\infty}^{\infty} 2\,\mathrm{Im}\Big[A_{p,2}^*c_{q,m,n}^{RE}\tilde{S}_{RE}^{(3)}(\omega_{q,m,n}^{RE},\omega_{m,n}^{RE},\omega_n^{RE}) \times e^{-i(-p+q+m-n)\Delta\omega_r t}\left\{e^{i(-p+q)\Delta\omega_r t} + e^{i(-p+m)\Delta\omega_r t}\right\}$$
$$+ A_{p,2}^*c_{q,m,n}^{NR}\tilde{S}_{NR}^{(3)}(\omega_{q,m,n}^{NR},\omega_{m,n}^{NR},\omega_n^{NR}) \times e^{-i(-p+q-m+n)\Delta\omega_r t}\left\{e^{i(-p+q)\Delta\omega_r t} + e^{i(-p+n)\Delta\omega_r t}\right\}\Big]$$

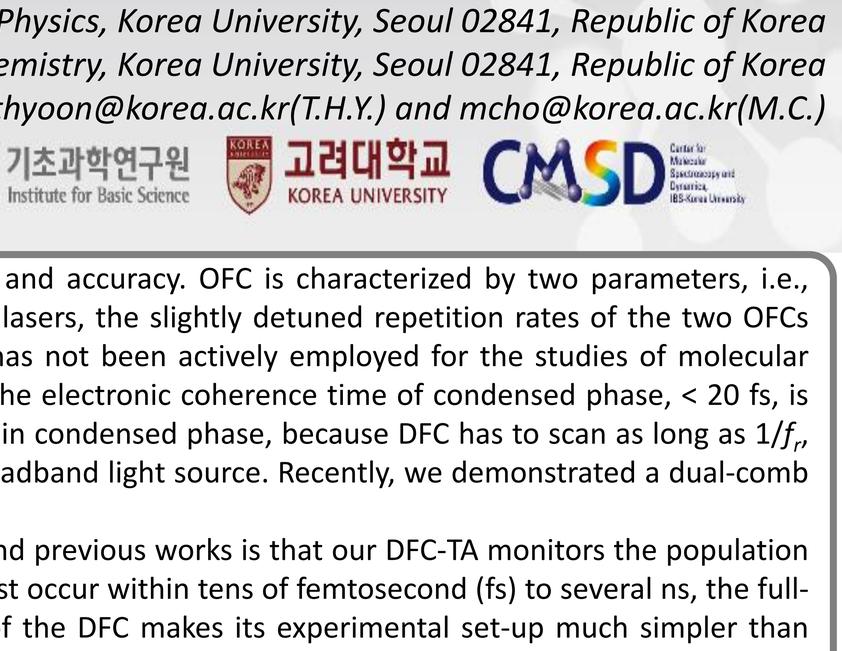
Due to the slow response of PD or the use of low-pass filters, the quickly oscillating terms in the signal must be eliminated. Then the relation between the indices becomes

[RE] $-p+q+m-n$
[NR] $-p+q-m+n$

Finally, we get

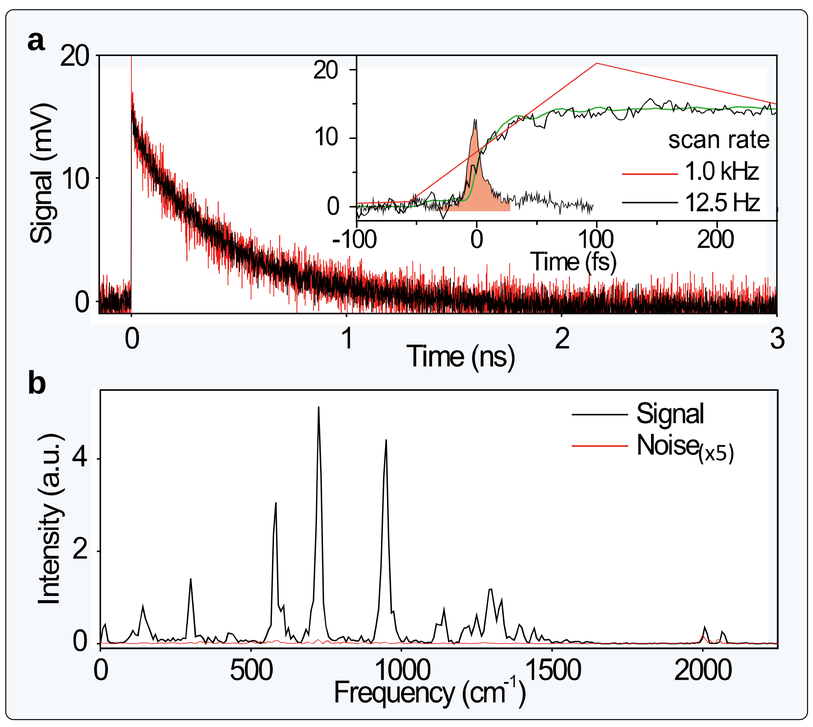
$$S_{DFC-TA}(t) \propto \sum_{q,m,n=-\infty}^{\infty} 2\,\mathrm{Im}\Big[A_{q+m-n,2}^*c_{q,m,n}^{RE}\tilde{S}_{RE}^{(3)}(\omega_{q,m,n}^{RE},\omega_{m,n}^{RE},\omega_n^{RE}) \times\left\{e^{-i\omega_{m,n}^{RE}f_D t} + e^{-i(q-n)\Delta\omega_r t}\right\}$$
$$+A_{q-m+n,2}^*c_{q,m,n}^{NR}\tilde{S}_{NR}^{(3)}(\omega_{q,m,n}^{NR},\omega_{m,n}^{NR},\omega_n^{NR}) \times\left\{e^{-i\omega_{m,n}^{NR}f_D t} + e^{-i(q-m)\Delta\omega_r t}\right\}\Big]$$

Experiment



The schematic diagram of 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 and recorded with a sampling rate of f_r. LO: local oscillator, PD: photodetector, BS: beam splitter.

Results



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, which resolves the vibrational frequency upto 1500 cm^{-1}. The noise spectrum (red) were obtained from the DFC-TA data at -5 ps to -1 ps.The fast scan rate and high time-resolution of DFC-TA would be applied for various unexplored chemical reactions. Recently, we have succeed to spread DFC-TA into frequency domain with a few second of scan rate.

[1] *J. Phys. Chem. Lett.* **2018**, 9, 1866-1871