Dual-Frequency Comb Nonlinear Spectroscopy: Direct Measurement of Correlation between Molecular Structure and Reaction Kinetics

JunWoo Kim[1], Tai Hyun Yoon[1,2,*] and Minhaeng Cho[1,3,*]

Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Seoul 02841, South Korea
Department of Physics, Korea University, Seoul 02841, South Korea
Department of Chemistry, Korea University, Seoul 02841, South Korea
*thyoon@korea.ac.kr, mcho@korea.ac.kr

Introduction

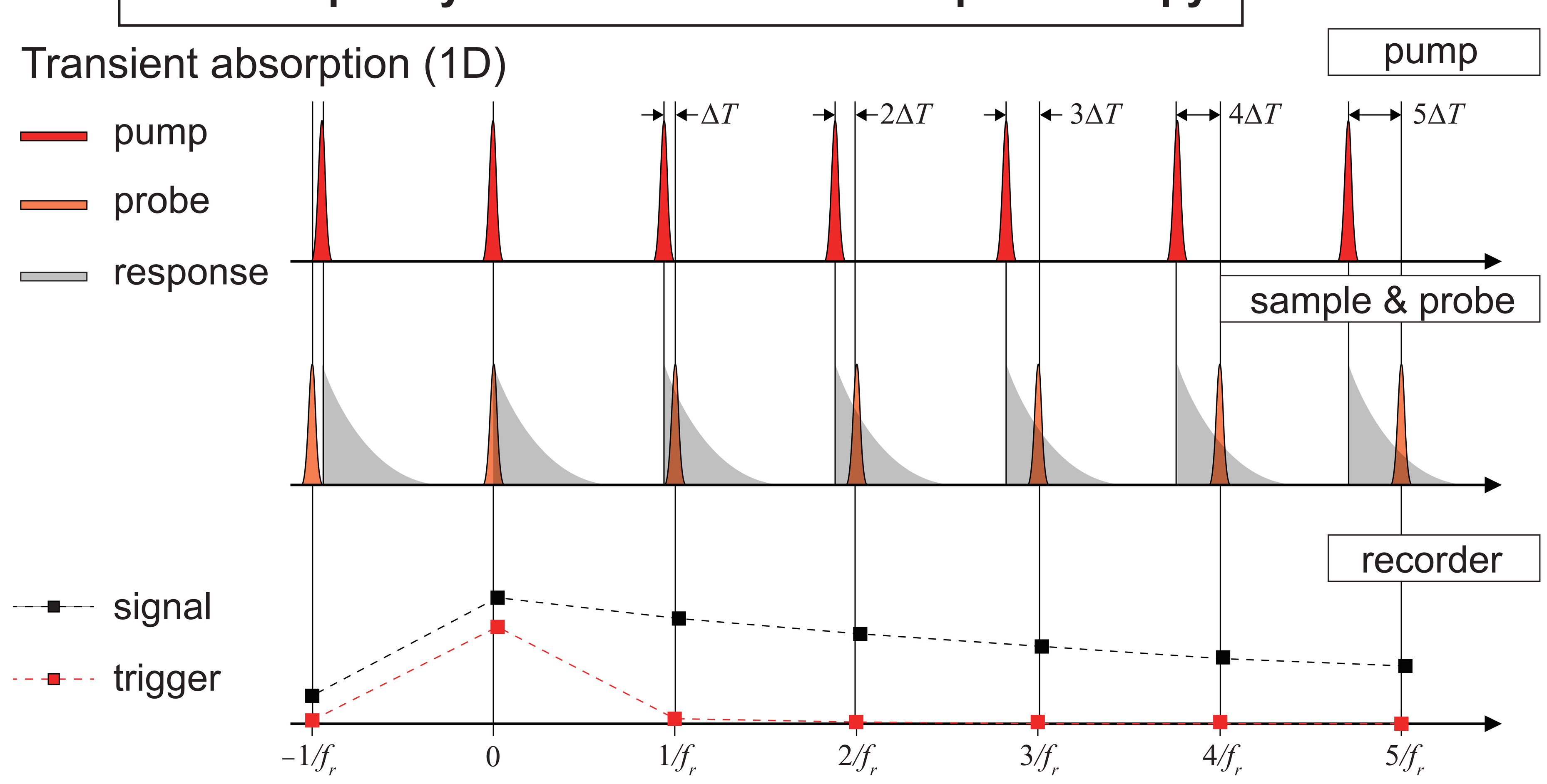
Time-resolved spectroscopy has been revolutionarily developed in last four decades to unveil the secrets of complex photochemical systems in nature. In particular, femtosecond light source provides not only the femtosecond-time resolution but also the molecular structure of photochemical species. In these days, to obtain those information, many femtosecond experiments are designed based on optically-amplified laser systems with low-repetition-rate (~kHz), mechanical time-delay line and photodetector array. This instrumentation is advantageous for observing the frequency-resolved nonlinear response of molecules in condensed phase at early waiting time below picosecond time scale, but much invaluable information across picosecond to nanosecond range is missing unintendedly.

Dual frequency-comb (DFC) is a set of two frequency-stabilized lasers with equally-spaced spectral lines. When the repetition rates of the two lasers are slightly detuned as fr and $f_r + \Delta f_r$, the time-delay between the two lasers (T) increases as much as ΔT precisely for every repetition period ($1/f_r$), where ΔT can be written as $\Delta T = \Delta f_r / f_r^2$. Then, DFC scans T from zero to $1/f_r$, which is tens of ns in general, with the scan- and sampling-rates of Δfr, which ranges from tens of Hz to several kHz, and f_r, respectively. If the carrier-envelope offset frequencies of DFC system are also stabilized, DFC can measure the electronic coherence of optical samples. This enables DFC to be applied gas-phase spectroscopy and atmospheric analysis, which requires the frequency resolution of GHz level. We have applied the unique properties of DFC to nonlinear spectroscopy in condensed-phase [1, 2], and theoretically described it based on time-dependent perturbation theory [3]. Furthermore, we have recently succeeded to expand DFC-based time-resolved spectroscopy into two-dimensional spectroscopy.

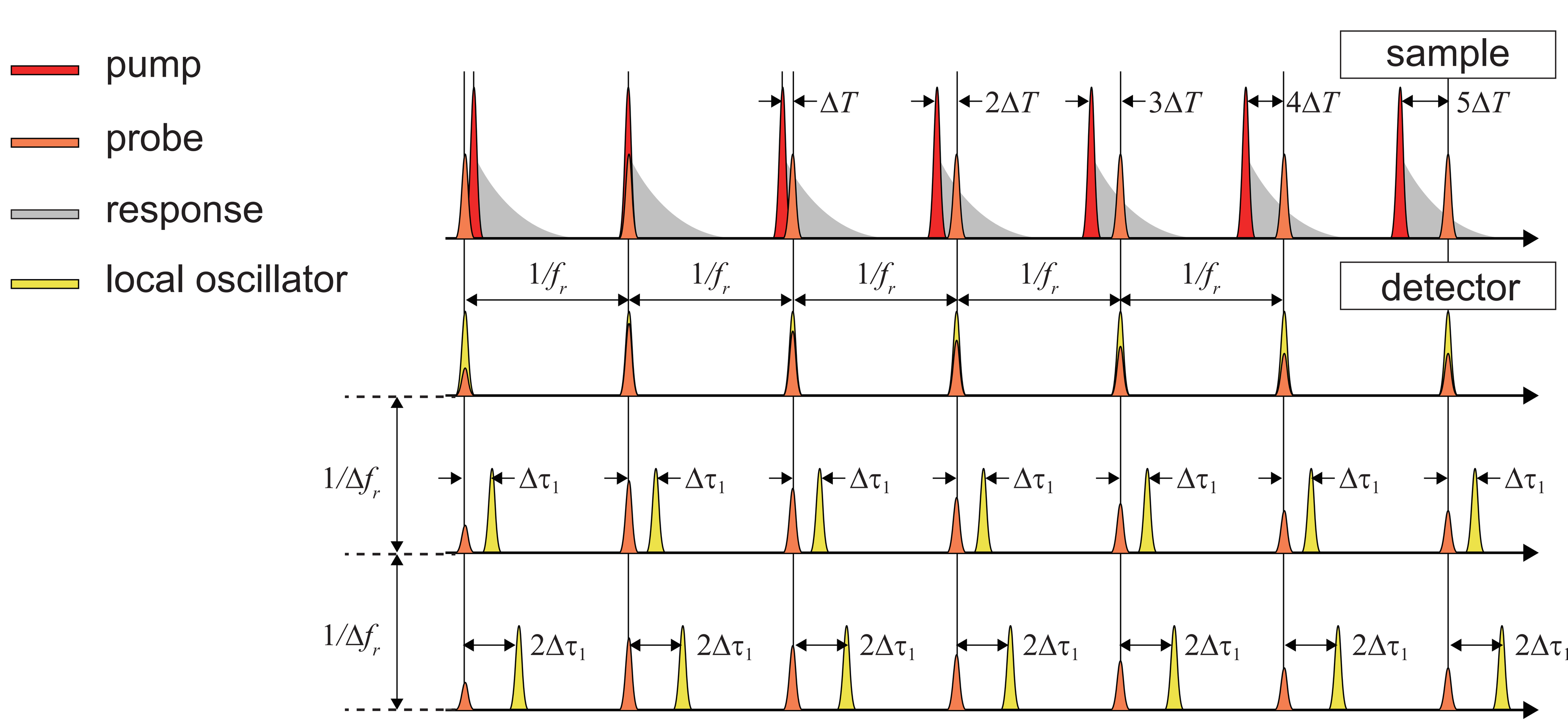
[1] JW. Kim, B. Cho, T. H. Yoon and M. Cho, *J. Phys. Chem. Lett.*, **9**, 1866-1871 (2018)
[2] JW. Kim, T. H. Yoon and M. Cho, *J. Phys. Chem. B*, **122**, 9775-9785 (2018)
[3] JW. Kim, J. Jeon, T. H. Yoon and M. Cho, *Chem. Phys.*, **520**, 122-137 (2019)

Dual Frequency Comb Time-Resolved Spectroscopy

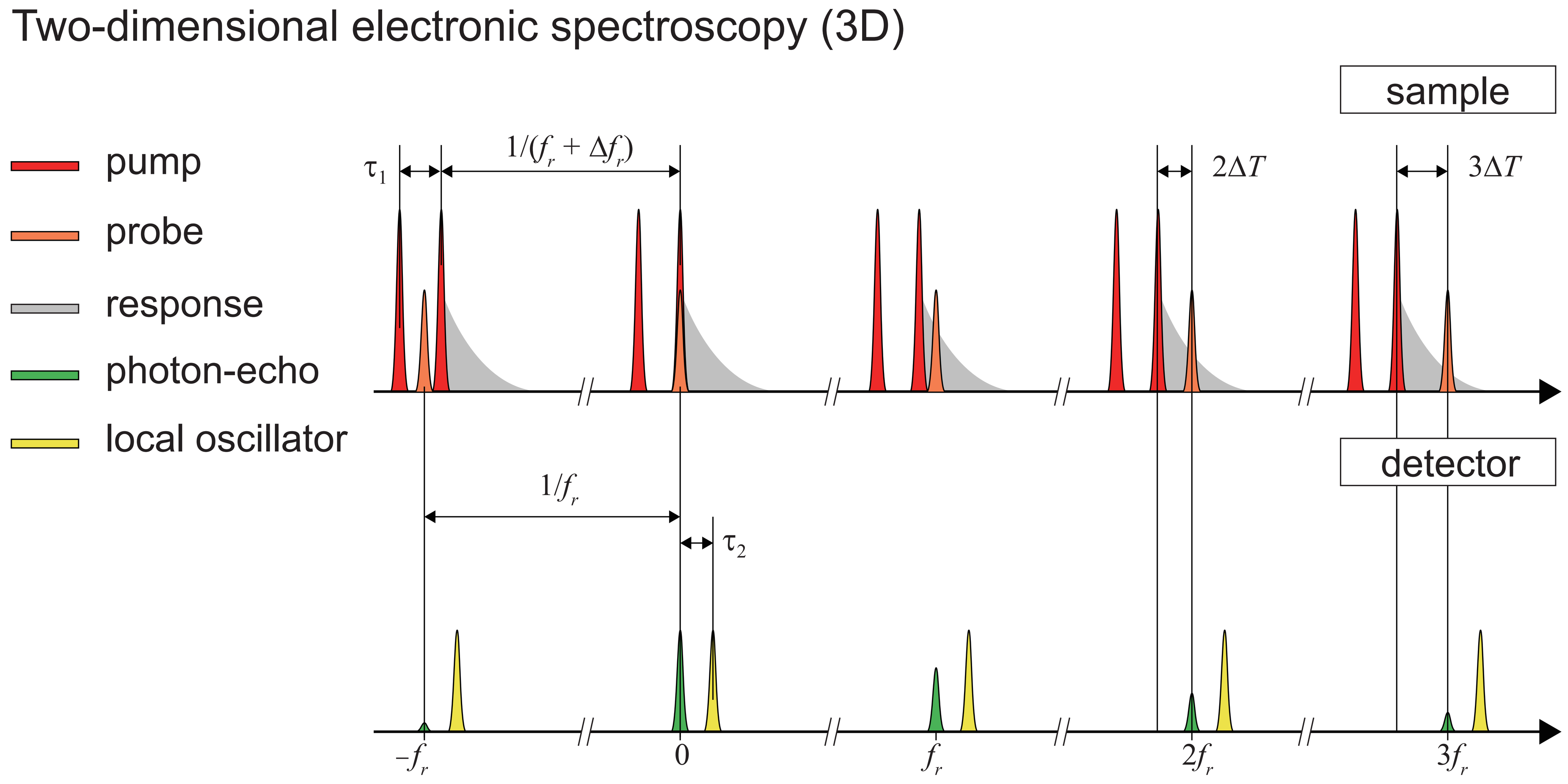
Transient absorption (1D)



Transient absorption spectroscopy (2D)

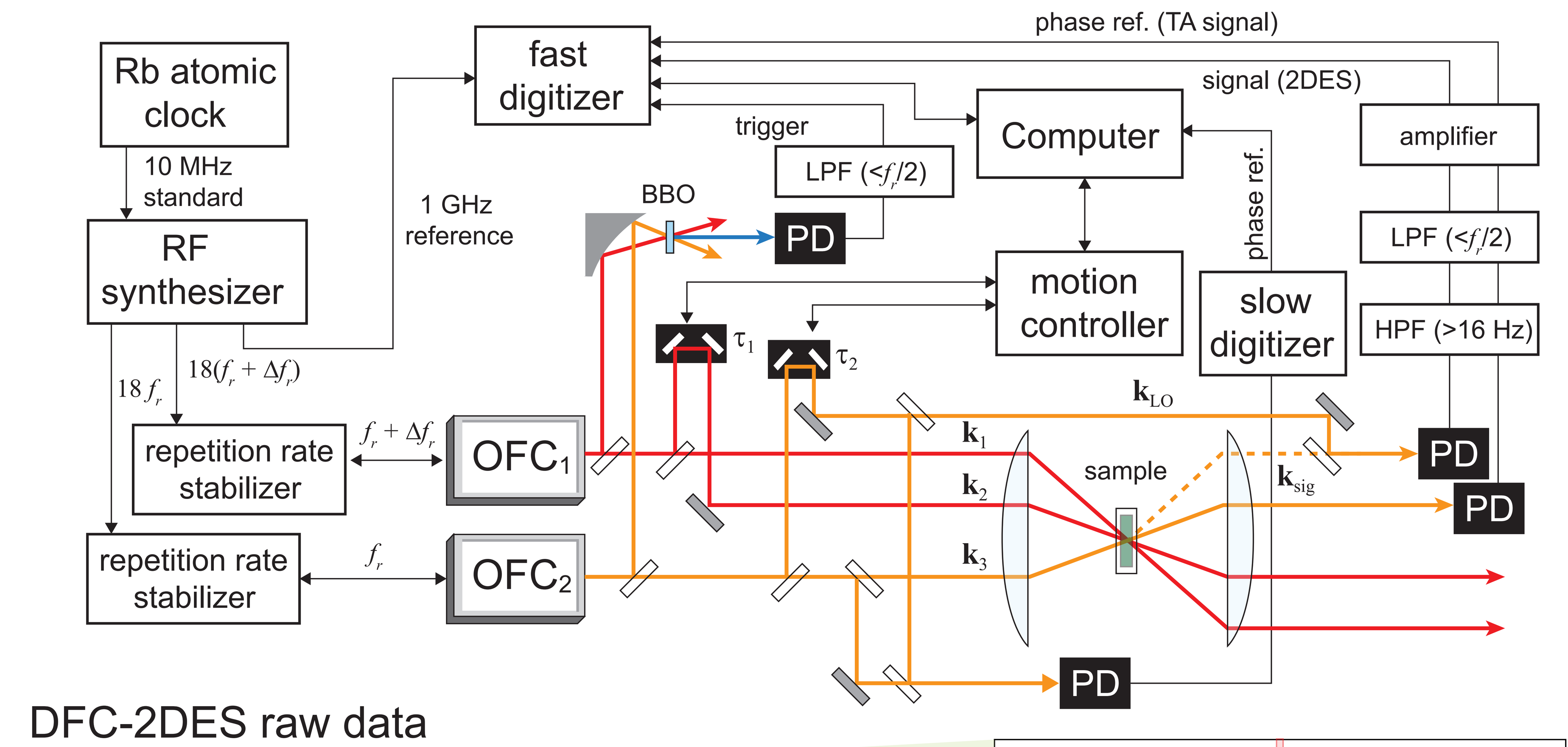


Two-dimensional electronic spectroscopy (3D)

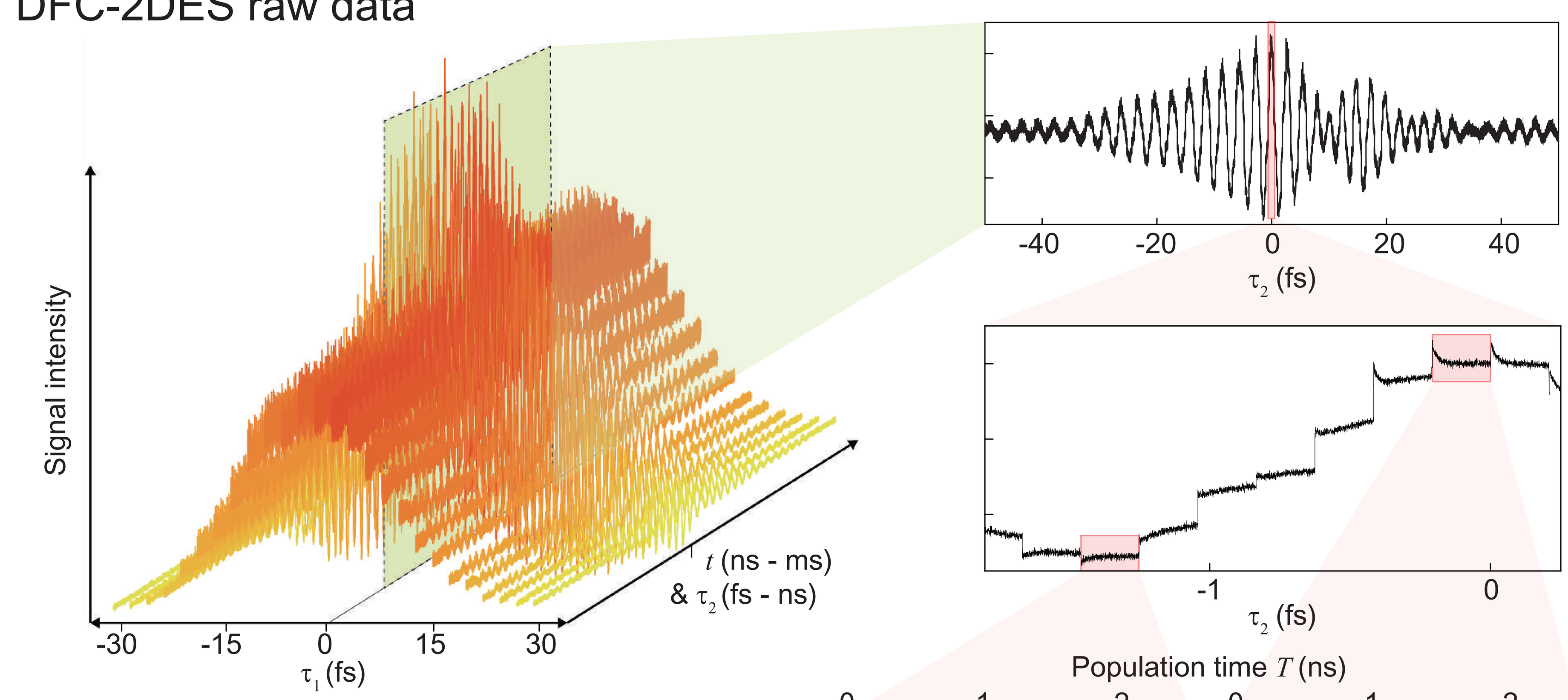


RF domain Data Acquisition with Single-Point Photodetectors

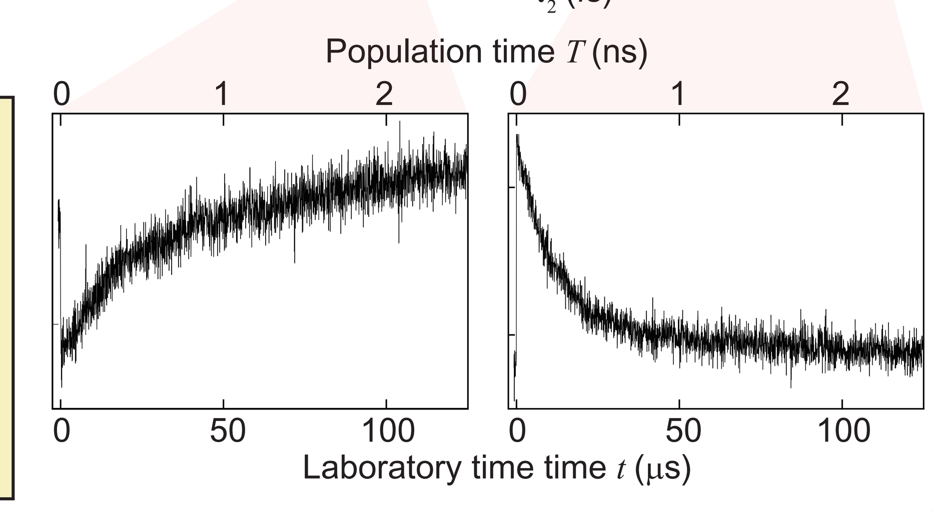
Instrumentation of DFC-2DES



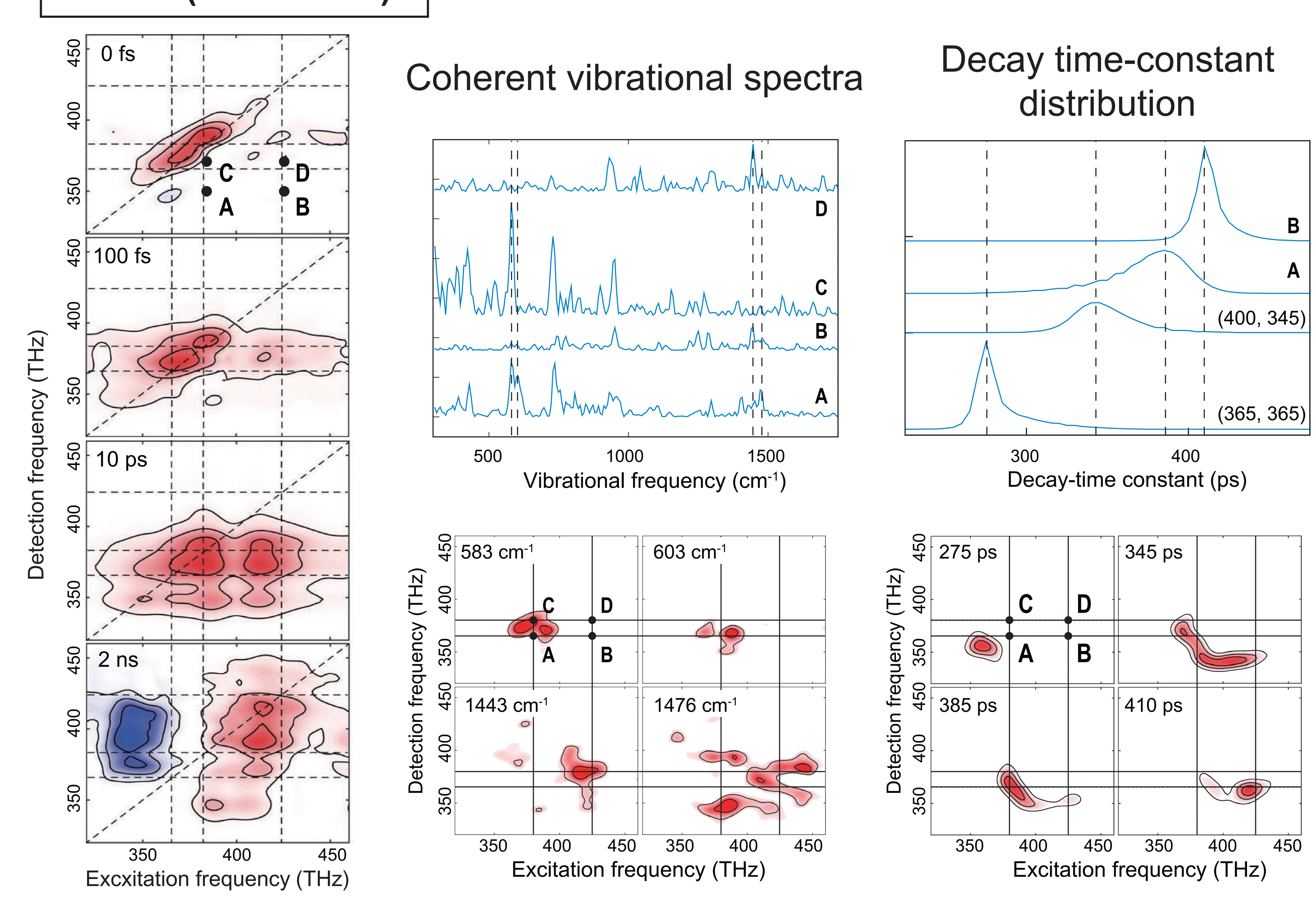
DFC-2DES raw data



(1) T: automatic scaned by repetition frequency detuning Δf_r, where Δf_r = 32 Hz, 3.2 kHz (ΔT = 5 fs, 500 fs)
(2) τ_2: continuously scanned while T is being scanned
(3) τ_1: fixed
(4) Phase-errors with respect to τ_1 and τ_2 are analytically calibrated by two references.
(5) Gated sampling
(6) Simultaneous multi-channel measurement



Result (DFC-2DES)



Theory

Frequency comb field (1)

$$E_j(\mathbf{r},t) = e^{i\mathbf{k}_j(\omega_{c,j})\cdot\mathbf{r} - i\omega_{c,j}t} \sum_{n=-\infty}^{\infty} A_{n,j} e^{-in\omega_{r,j}t}$$

$$\omega_{r,2} - \Delta\omega_r = \omega_{r,1}$$

Third-order polarization (2)

$$\begin{aligned}
P^{(3)}(\mathbf{r},t,\tau_1) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \\
S_{RE}^{(3)}(t_3,t_2,t_1)\Big\{ & E_2(\mathbf{r},t-t_3)E_1(\mathbf{r},t-t_3-t_2)E_1^*(\mathbf{r},t+\tau_1-t_3-t_2-t_1) \\
& + E_1(\mathbf{r},t-t_3)E_2(\mathbf{r},t-t_3-t_2)E_1^*(\mathbf{r},t+\tau_1-t_3-t_2-t_1)\Big\} \\
+ S_{NR}^{(3)}(t_3,t_2,t_1)\Big\{ & E_2(\mathbf{r},t-t_3)E_1^*(\mathbf{r},t-t_3-t_2)E_1(\mathbf{r},t+\tau_1-t_3-t_2-t_1) \\
& + E_1(\mathbf{r},t+\tau_1-t_3)E_1^*(\mathbf{r},t-t_3-t_2)E_2(\mathbf{r},t-t_3-t_2-t_1)\Big\}
\end{aligned}$$

Inserting (1) into (2)

$$\begin{aligned}
P^{(3)}(\mathbf{k}_{sig},t,\tau_1) \propto i e^{i\mathbf{k}_{sig}\cdot\mathbf{r}} \sum_{q,m,n=-\infty}^{\infty} \Big[& c_{q,m,n}^{RE} \tilde{S}_{RE}^{(3)}(\omega_{q,m,n}^{RE}, \omega_{m,n}^{RE}, \omega_n^{RE}) e^{-i\omega_{q,m,n}^{RE}t - i(m-n)\Delta\omega_r t - i\omega_n^{RE}\tau_1} \\
& + c_{q,m,n}^{NR} \tilde{S}_{NR}^{(3)}(\omega_{q,m,n}^{NR}, \omega_{m,n}^{NR}, \omega_n^{NR}) e^{-i\omega_{q,m,n}^{NR}t - i(-m+n)\Delta\omega_r t - i\omega_n^{NR}\tau_1} \Big]
\end{aligned}$$

Interference between photon-echo signal and local oscillator

$$\begin{aligned}
I(\tau_2,t,\tau_1) &= |E_2(t-\tau_2) + E^{(3)}(t,\tau_1)|^2 \\
&= |E_2(t-\tau_2)|^2 + |E^{(3)}(t,\tau_1)|^2 + 2\,\mathrm{Re}[E_2^*(t-\tau_2)E^{(3)}(t,\tau_1)]
\end{aligned}$$

DFC-2DES signal

$$\begin{aligned}
I(\tau_2,t,\tau_1) \propto \sum_{q,m,n=-\infty}^{\infty} \mathrm{Im}\Big[& A_{q+m-n}^* c_{q,m,n}^{RE} \tilde{S}_{RE}^{(3)}(\omega_{q,m,n}^{RE}, \omega_{m,n}^{RE}, \omega_n^{RE}) e^{-i\left[\omega_{q,m,n}^{RE}\tau_2 + (m-n)\Delta\omega_r t + \omega_n^{RE}\tau_1\right]} \\
& + A_{q-m+n}^* c_{q,m,n}^{NR} \tilde{S}_{NR}^{(3)}(\omega_{q,m,n}^{NR}, \omega_{m,n}^{NR}, \omega_n^{NR}) e^{-i\left[\omega_{q,m,n}^{NR}\tau_2 + (-m+n)\Delta\omega_r t + \omega_n^{NR}\tau_1\right]} \Big]
\end{aligned}$$