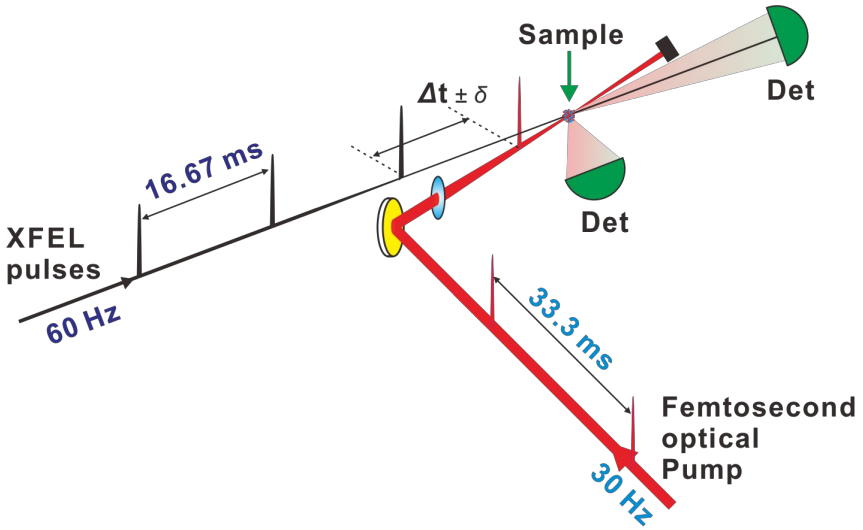
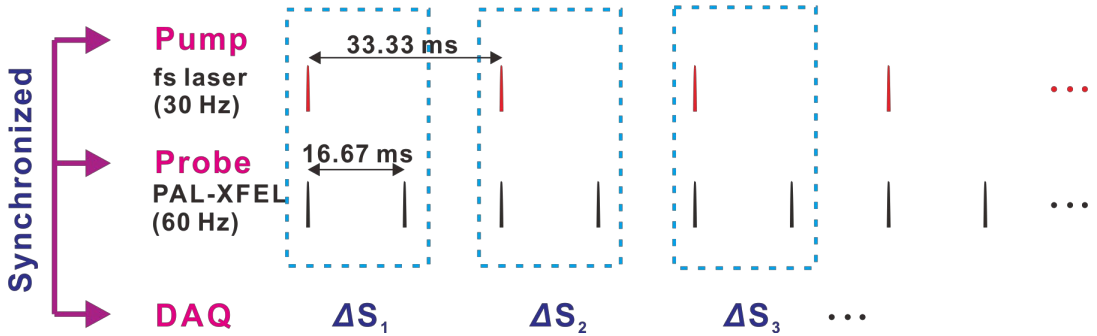
Ultrafast absorption spectroscopy

레이저그룹

엄인태

Time-resolved XFEL experiments, and optical laser





Time-resolved diffraction of Bi_2Se_3

by prof. Hyunjuing Kim's group **Nano letters (2021)**

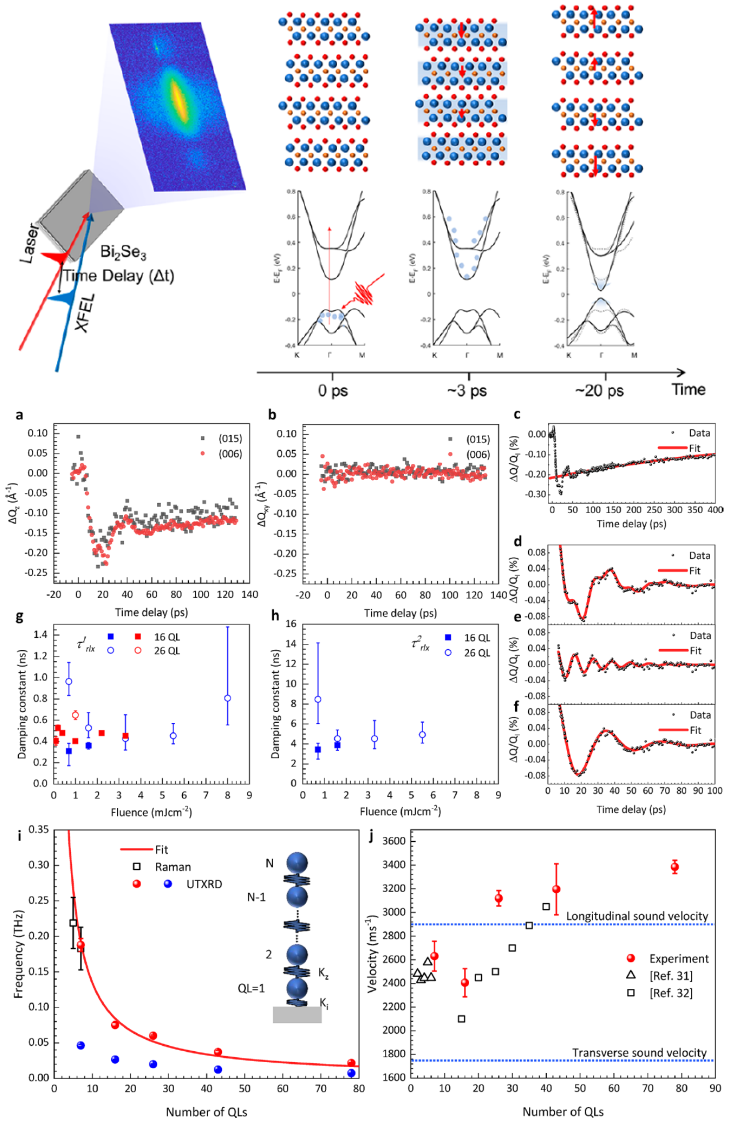


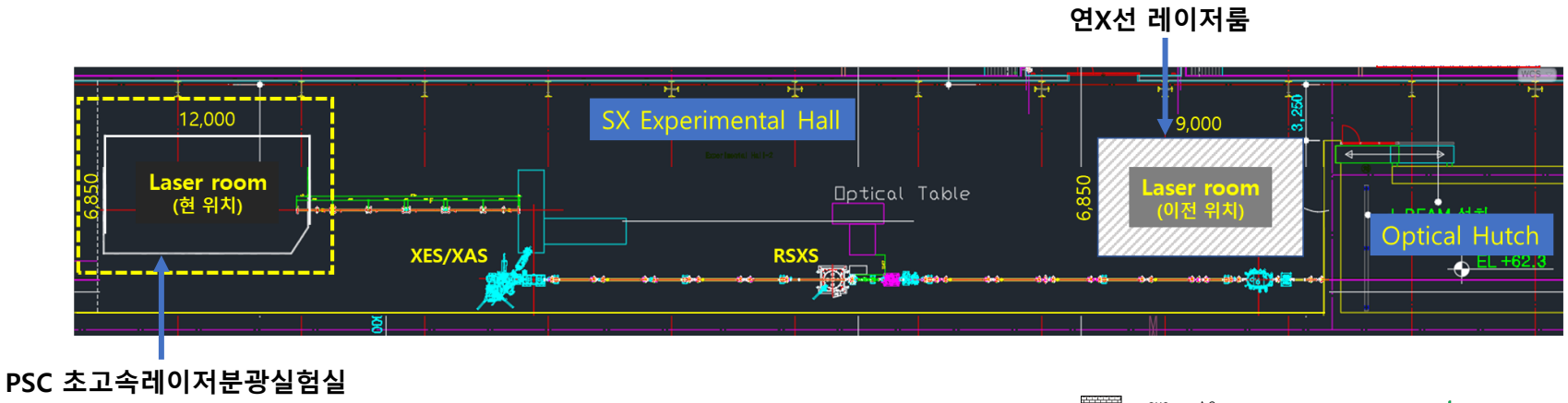
Figure 2. Interlayer vibration modes and relaxation fits to strain curves. (a,b) Position change of the (006) and (015) Bragg peaks in the Q_z and Q_{xy} directions. (c–f) Example of the steps in a strain-curve fitting with a 16 QL sample and 1.0 mJ cm^{-2} fluence; see text for details. (g) Relaxation damping constant τ^1_{rlx} for 16 QL (closed squares) and 26 QL (open circles). The red and blue symbols correspond to the values derived from data obtained at XFEL and the synchrotron source, respectively. (h) τ^2_{rlx} for 16 QL (squares) and 26 QL (circles) derived from data obtained at the synchrotron. (i) Oscillation frequencies for the breathing (red) and interface (blue) modes for Bi_2Se_3 films with different thicknesses. The error bars denote the 95% confidence intervals. The measured Raman frequencies are plotted as squares. The solid red line represents the fit to the breathing mode model. (j) Propagation velocities for the breathing mode are plotted as blue circles. The error bars denote the 95% confidence intervals. The triangle and square represent the measurements obtained by Raman spectroscopy (ref 31) and ultrafast laser reflection (ref 32), respectively.

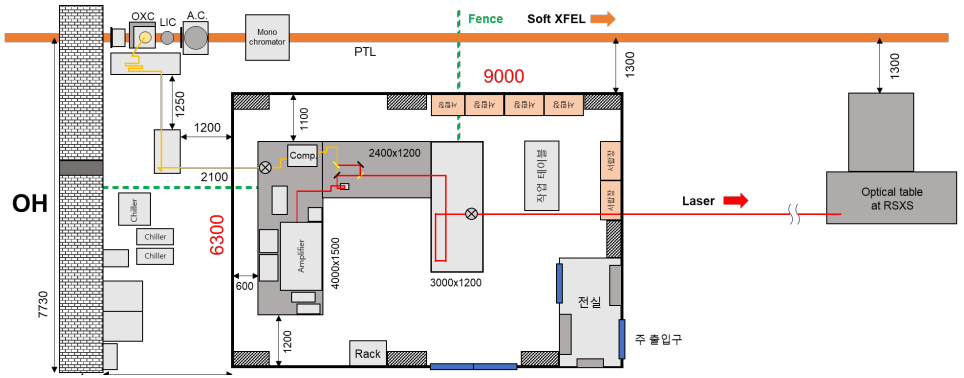
PSC 초고속 레이저 분광 실험실 (130-2호)

- **구축 목적**
  - **레이저와 XFEL을 통한 상호보완적인 분광학 연구**
  - **레이저 실험환경 구축을 통한 XFEL 연구 활성화**

    펨토초레이저를 이용한 off-line 실험환경을 통해 XFEL 빔라인 실험을 보완, 촉진

    극초고속 동역학 연구 활성화를 통해 XFEL 실험에 대한 접근성 증가

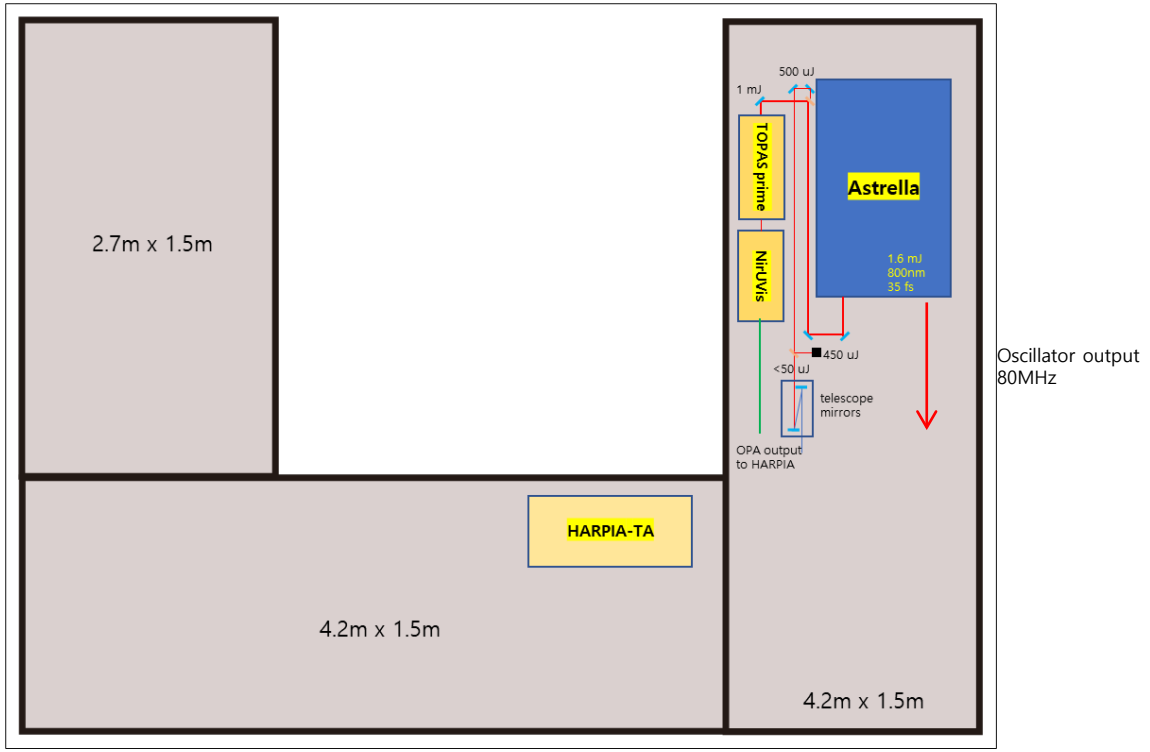




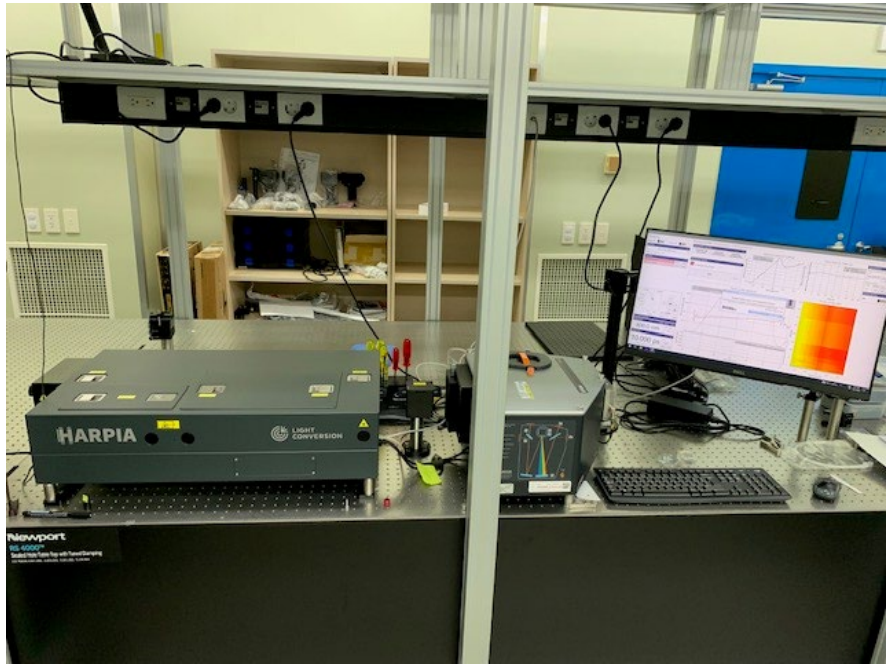
PSC 초고속 레이저 분광 실험실 : 레이저시스템 사양

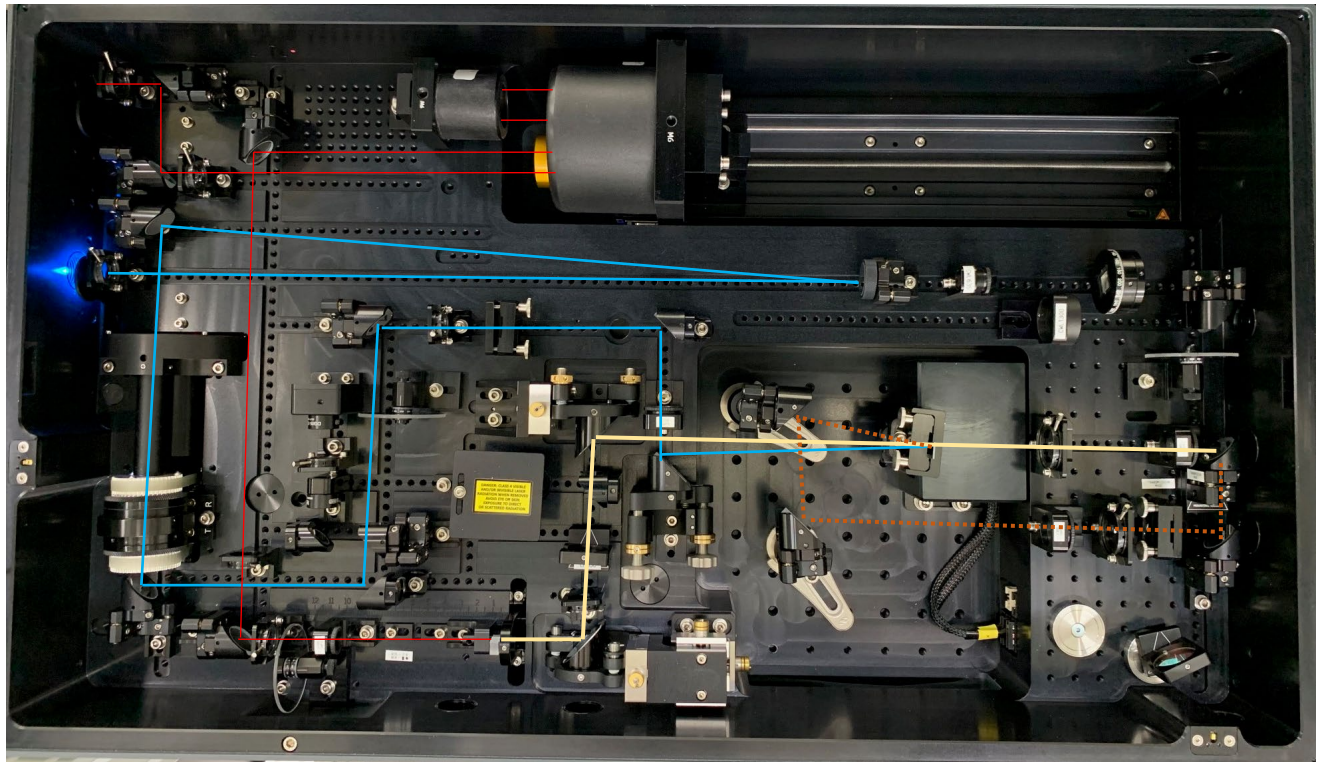
▶ Ti:Sapphire regenerative amplifier system : **Astrella (Coherent)**

- Pulse energy : > 1.6 mJ/pulse after compression
- Repetition rate : 5 kHz (max)
- Pulse duration (800 nm) : <35 fs
- Frequency tuning : OPA (240 - 2600 nm) : **TOPAS prime (Light conversion)**



PSC 초고속 레이저 분광 실험실 : Pump-probe absorption spectrometer



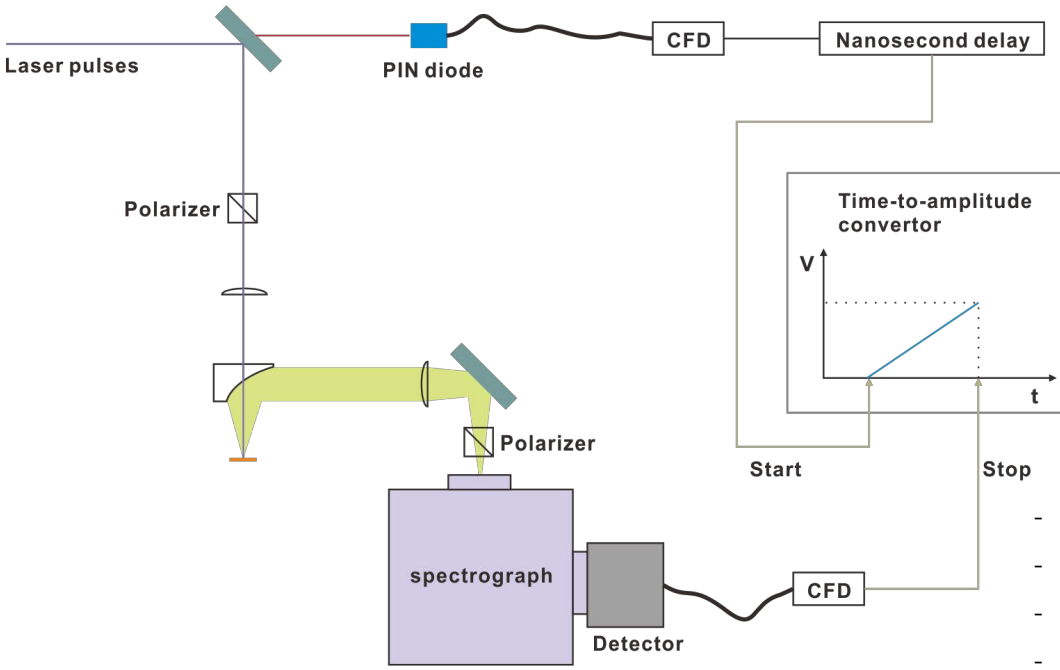


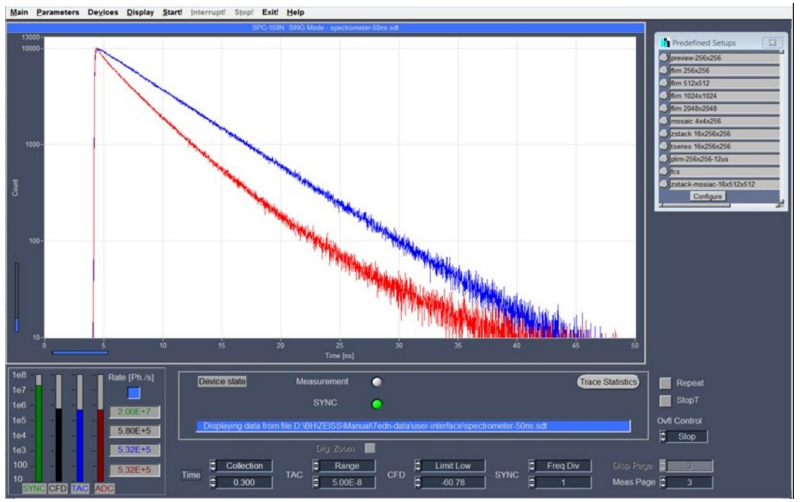
- **Specifications**
  - Pump wavelength: Ti:Sapphire / OPA
  - Probe excitation wavelength: 800 nm
  - Probe wavelength range: 330 ~ 1400nm (CaF_2, rep. rate<2 kHz)
    450 ~ 1400nm (Al_2O_3)
  - Detector: photodiode array (256 pixels) with spectrograph (f=300 mm)
  - Spectral range of multichannel detectors: 200~1100 nm, 700~1800 nm
  - Time resolution: <1.4 x pump or probe pulse duration, whichever is longer

  - Motorized sample holder
  - **Reflection mode support (switchable between reflection & transmission)**
  - Pump polarization control

PSC 초고속 레이저 분광 실험실 : Time-resolved Photoluminescence

Time-correlated single photon counting





- Time channel width down to 407 fs
- Electrical time resolution 3.5 ps FWHM
- 10 MHz saturated count rate
- Timing jitter <0.4 ps

- Hybrid detector with a typical time resolution of 40 ps
- Peak detection at 500 nm
- Active area of 20 um dia.
- Dark count <7 cps

Article review: Ultrafast spectroscopy – State of the art and open challenges

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Ultrafast Spectroscopy: State of the Art and Open Challenges

Margherita Maiuri,[†] Marco Garavelli,[‡] and Giulio Cerullo*,[†]

[†]IFN-CNR, Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy
[‡]Dipartimento di Chimica Industriale, Università degli Studi di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy

ABSTRACT: Ultrafast spectroscopy techniques use sequences of ultrashort light pulses (with femto- to attosecond durations) to study photoinduced dynamical processes in atoms, molecules, nanostructures, and solids. This field of research has experienced an impetuous growth in recent years, due to the technological progress in the generation of ultrashort light pulses and to the development of sophisticated spectroscopic techniques, which greatly increase the amount of information on the process under study. This paper aims at providing a non-exhaustive overview of the state of the art of the field and at pointing out future challenges. We first review the progress in ultrafast optics, which has enabled the generation of broadly tunable light pulses with duration down to a few optical cycles; we then discuss the pump–probe technique, showing examples of its capability to combine very high time resolution, down to the attosecond regime, with broad spectral coverage; we introduce two-dimensional spectroscopy and present results that demonstrate the additional information content provided by the combination of temporal and spectral resolution. Next, we review the achievements of ultrafast X-ray and electron diffraction, which provide time-dependent structural information on photochemical processes, and we conclude with a critical analysis of the future open challenges in the field.

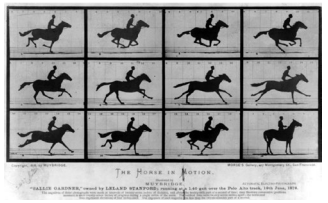
flashes. Stroboscopic photography, introduced by Harold E. Edgerton in the mid 20th century,[1] brought the time resolution down to the microsecond range. Short light pulses can be used not only to monitor, but also to initiate a dynamical process. The "pump-probe" technique, pioneered by Abraham and Lemoine in 1899,[2] employs two synchronized light pulses: the excitation or "pump" pulse, which triggers a photoinduced phenomenon, and a delayed "probe" pulse, which measures a time-dependent variation of an optical property of the sample, such as absorption or reflection. In 1949, Norrish and Porter[3] used a variant of the technique, known as flash photolysis, which combines two electronically delayed light flashes with milli- to microsecond duration, in order to measure long-lived transient intermediates of photochemical reactions, e.g., aromatic free radicals and triplet states. For their work, they received the Nobel Prize in Chemistry in 1967.

To estimate the time resolution required to follow a molecular process in real time, one can borrow the argument used by Ahmed Zewail in his 1999 Nobel Prize lecture on the development of femtochemistry.[4] Considering a typical interatomic distance d = 1 Å (10^{-10} m) and an average speed of motion of the atoms $v = 10^3$ m/s, one readily obtains that a time resolution $\Delta t = 10^{-13}$ s or better is required to visualize atomic dynamics. This time scale matches the periods of molecular vibrations, which, for frequencies in the 300–3000 cm^{-1} interval, range from ~100 to ~10 fs. While femtosecond light pulses are able to track atomic motions within molecules, much shorter light pulses are required to

The progress of ultrafast science

1878 1899 1950 1967 1974 1991 1999 2005 2009 2016

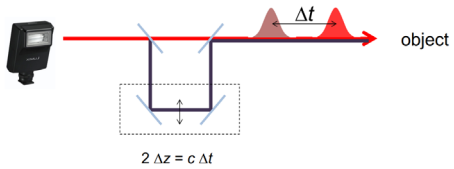
E. Muybridge



Multiple cameras with fast shutters

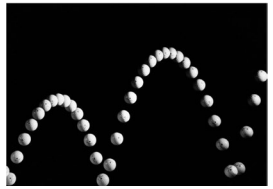
(~1 ms exposure times)

Abraham and Lemoine



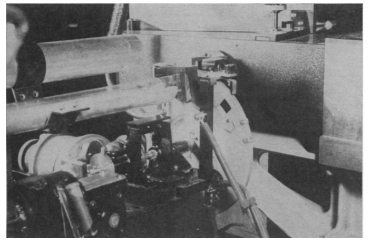
The first pump-probe with two synchronized light pulses and a delay line
: Kerr response of liquid CS_2
(tens of nanosecond time-domain)

Harold E. Edgerton



Stroboscopic photography with short light pulses (<1 us time resolution)

Norrish and Porter (The Nobel prize)



Flash photolysis
(us time resolution)
: Aromatic radicals, triplet states

The first femtosecond Laser (Dye)

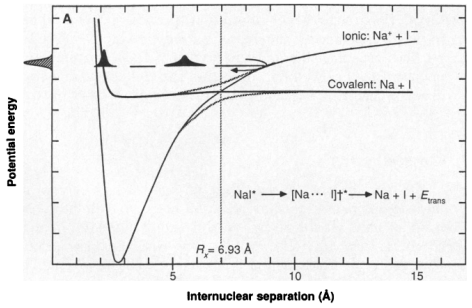
Ti:Sapphire femtosecond laser

LCLS

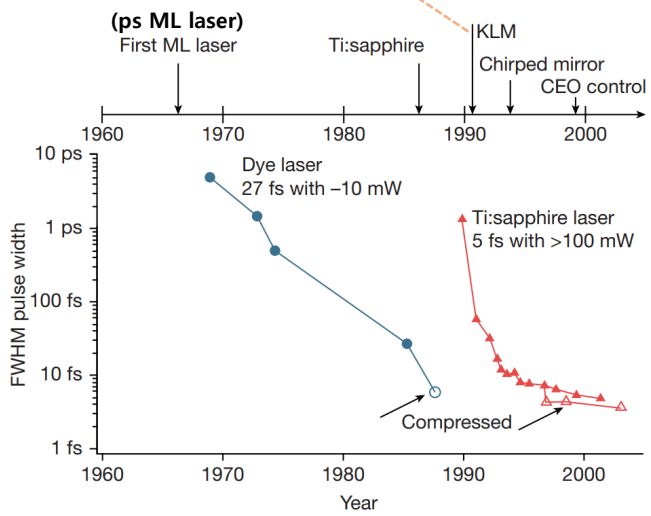
FLASH

PAL-XFEL

A. Zewail (The Nobel prize)

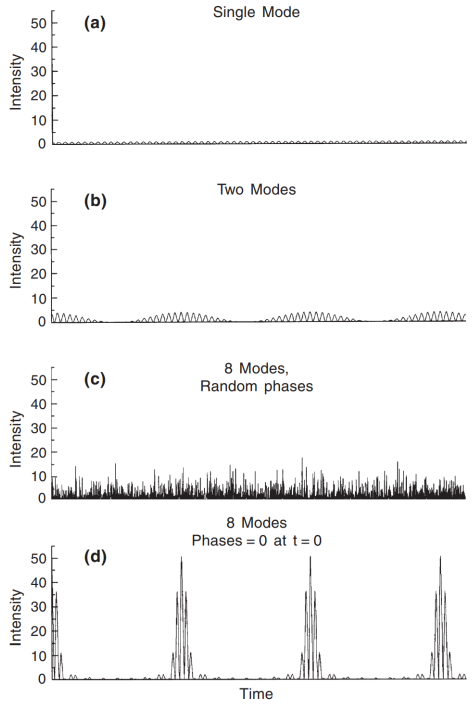


"Femtochemistry"
Chemical reactions in the femtosecond time scale



Ultrashort, intense and tunable pulse generation

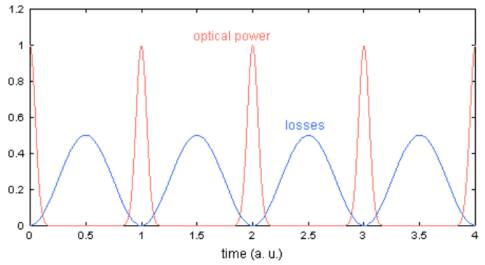
Mode-locking



Cavity length: ~189 cm

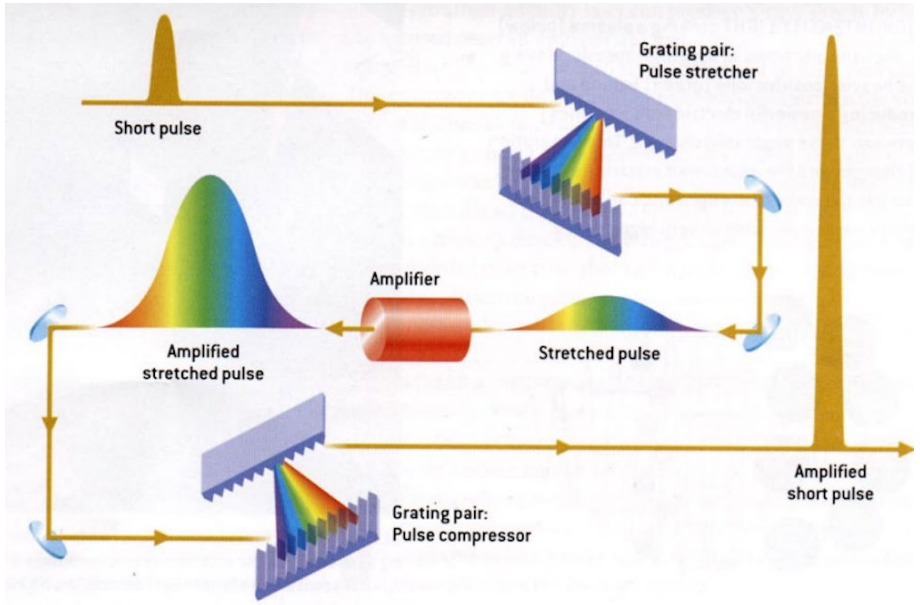
Full bandwidth of Ti:Sap output: ~100 nm

Number of longitudinal modes: ~600,000



Chirped pulse amplification

(The 2018 Nobel prize in physics)



Performance overview

Source	Wavelength	Pulse width	Pulse Energy	Repetition rate
Primary solid-state laser sources				
CPA Ti:sapphire	800 nm	5–20 fs	1–10 mJ	1 Hz-200 kHz
CPA Yb laser	1030 nm	150–300 fs	10 μJ – 1 mJ	1 kHz-10 MHz
Secondary sources by nonlinear frequency conversion				
Ti:sapphire-pumped OPA	450–3000 nm	5–100 fs	1 μJ-1 mJ	1–200 kHz
Yb-pumped OPA	390–3000 nm	5–200 fs	1–100 μJ	1 kHz-10 MHz
SHG, SFG	200–400 nm	10–200 fs	0.1–1 μJ	1–200 kHz
DFG	3–15 μm	30–200 fs	0.1–10 μJ	1–200 kHz
Terahertz	150–600 μm	1 ps	0.1nJ-1 μJ	1 kHz-100 MHz

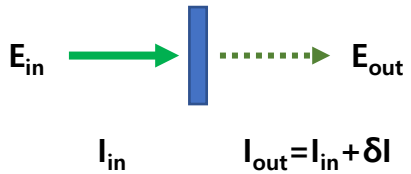
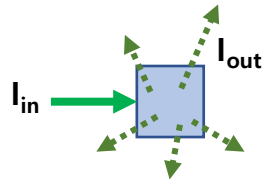
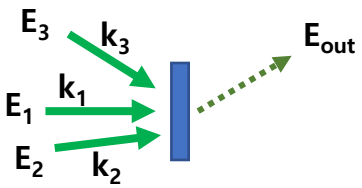
Nonlinear light-matter interaction

P: (induced) polarization density
E: external field
D: electric displacement
ε_0: electric permittivity
χ_e: electric susceptibility

$$\boldsymbol{P} = \varepsilon_0 \chi_e \boldsymbol{E} \qquad \boldsymbol{D} \equiv \varepsilon_0 \boldsymbol{E} + \boldsymbol{P}$$

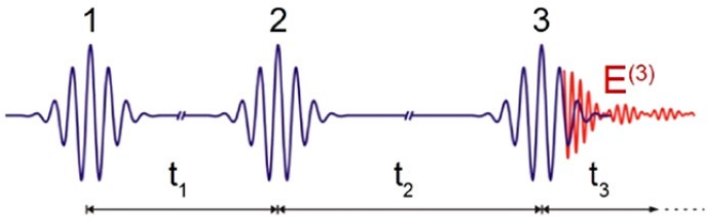
$$= \boldsymbol{P}_0 + \varepsilon_0 \chi^{(1)} \boldsymbol{E} + \varepsilon_0 \chi^{(2)} \boldsymbol{E} \cdot \boldsymbol{E} + \varepsilon_0 \chi^{(3)} \boldsymbol{E} \cdot \boldsymbol{E} \cdot \boldsymbol{E} + \varepsilon_0 \chi^{(4)} \boldsymbol{E}^4 + \varepsilon_0 \chi^{(5)} \boldsymbol{E}^5 + \cdots$$

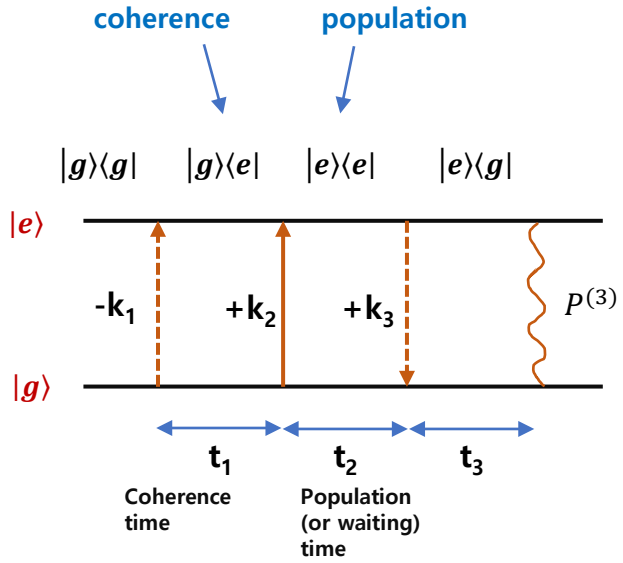
- $\varepsilon_0 \chi^{(1)} \boldsymbol{E}$: Linear optics, Index, Absorption
- $\varepsilon_0 \chi^{(2)} \boldsymbol{E} \cdot \boldsymbol{E}$: SHG, Parametric effects, ⋮
- $\varepsilon_0 \chi^{(3)} \boldsymbol{E} \cdot \boldsymbol{E} \cdot \boldsymbol{E}$: THG, Nonlinear index, ⋮

	Coherent	Spontaneous
Linear	Absorption  	Fluorescence, Raman, … 
Nonlinear	 	Fluorescence-detected NLS, etc.
	$I_{coherent} \propto \left\| \sum_i E_i \right\|^2$	$I_{incoherent} \propto \sum_i \|E_i\|^2$

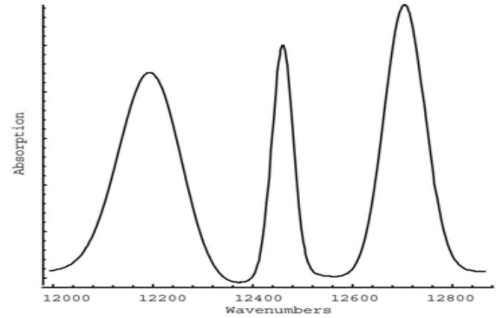
Two-dimensional spectroscopy

$$P^{(3)}(t_1,t_2,t_3) \xrightarrow{\text{FT}} P^{(3)}(t_1,t_2,\omega_3) \xrightarrow{\text{FT over } t_1} P^{(3)}(\omega_1,t_2,\omega_3)$$





Example of 2D spectrum

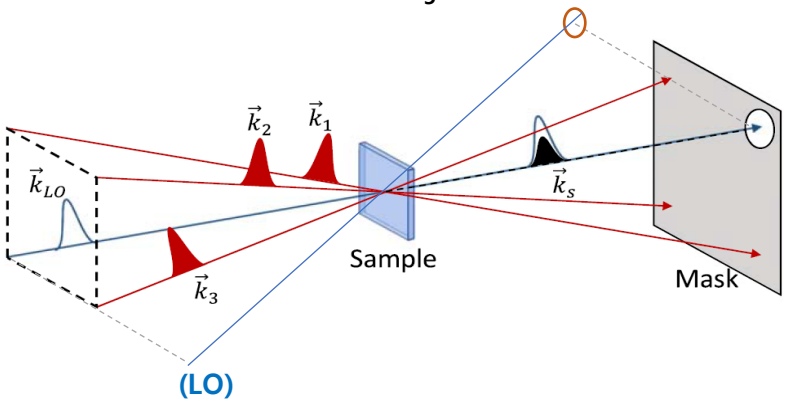


Diagonal
= 1D spectroscopy

-Photon echo

Rephasing

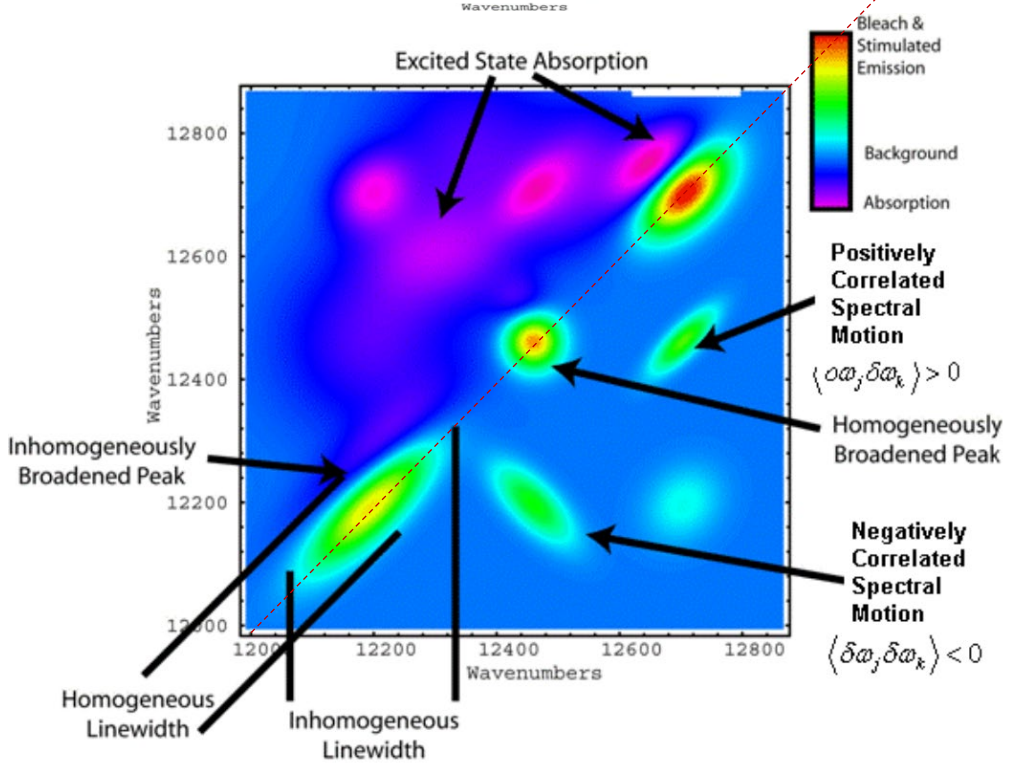
$k_{sig} = -k_1 + k_2 + k_3$



$k_{sig} = +k_1 - k_2 + k_3$

Non-rephasing

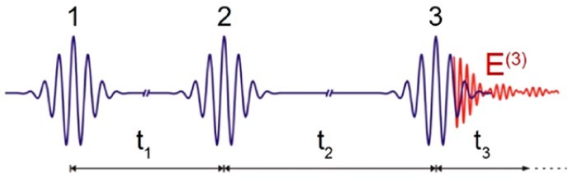
-Transient grating
(if t_1=0)



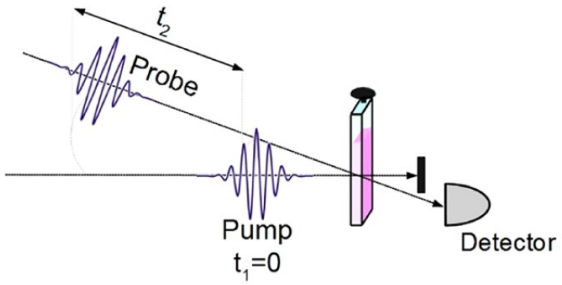
Optical heterodyne detection

$$I \propto \left[E_{\text{sig}}\cos(\omega_{\text{sig}}t+\varphi)+E_{\text{LO}}\cos(\omega_{\text{LO}}t)\right]^2 \propto \frac{1}{2}E_{\text{sig}}^2+\frac{1}{2}E_{\text{LO}}^2+2E_{\text{LO}}E_{\text{sig}}\cos(\omega_{\text{sig}}t+\varphi)\cos(\omega_{\text{LO}}t)$$

Transient absorption spectroscopy (Pump-probe)

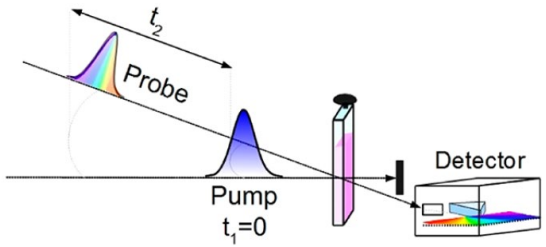


$t_1=0$
$k_1 = k_2 = k_{pu}$
$k_3 = k_{pr}$

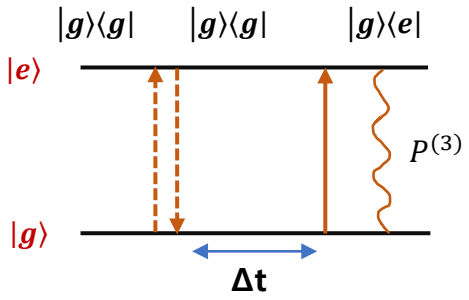


$k_{sig} = -k_{pu} + k_{pu} + k_{pr}$

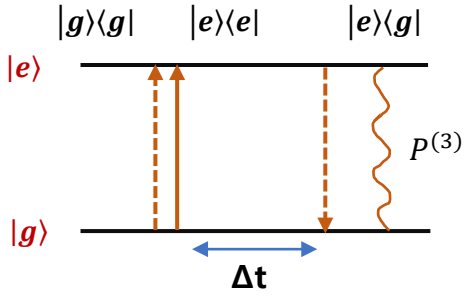
Self-heterodyne



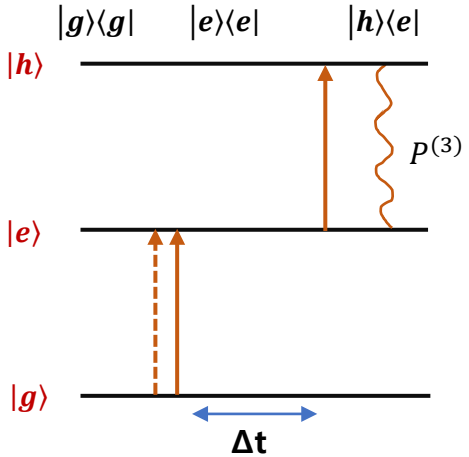
Ground state bleaching



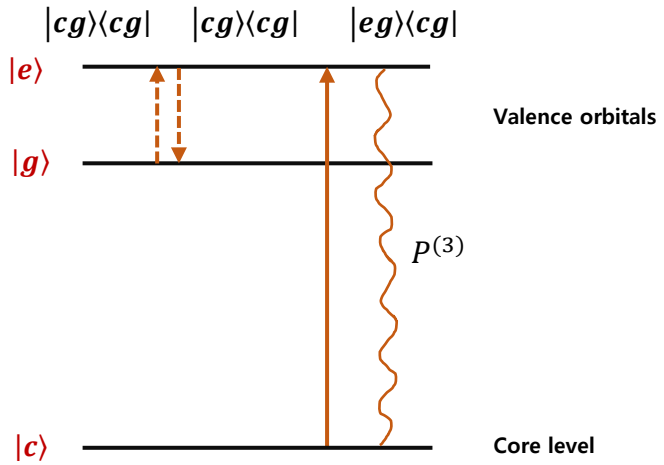
Stimulated emission

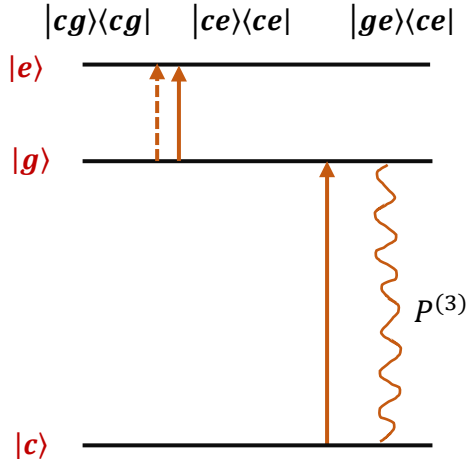


Excited state absorption



Optical pump & X-ray probe

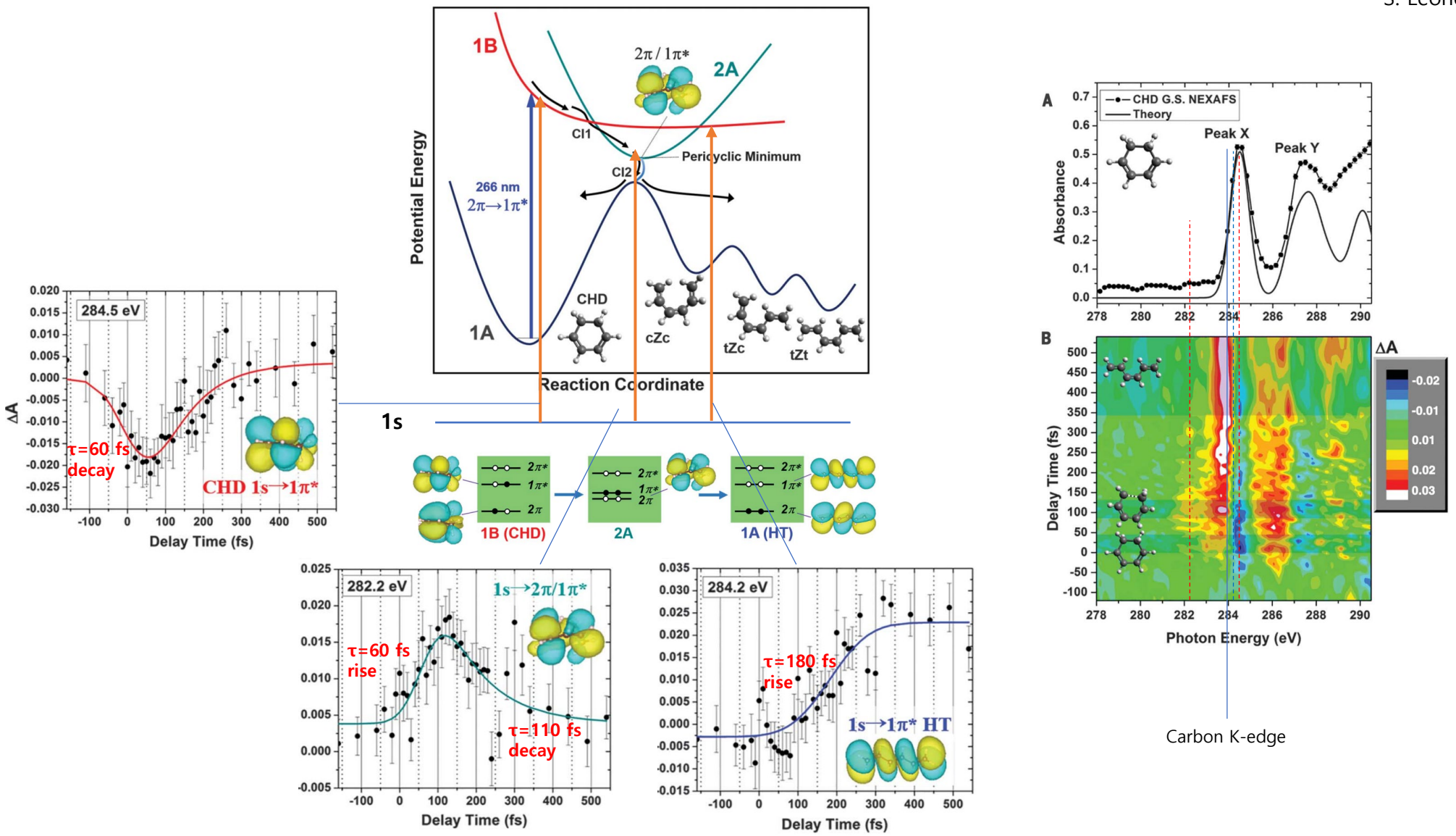




Experimental examples in the review article

Optical pump – EUV probe experiment for the ring opening reaction of 1,3-cyclobutadiene (CHD)

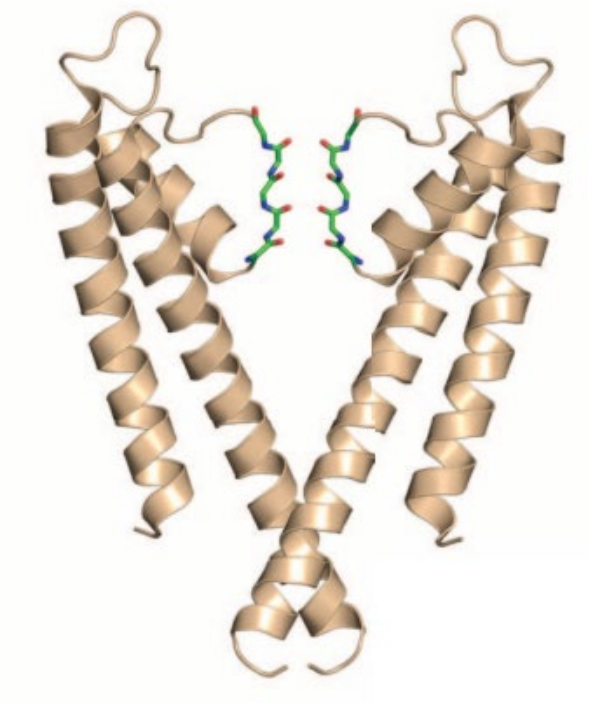
S. Leone et al., **Science** (2017)

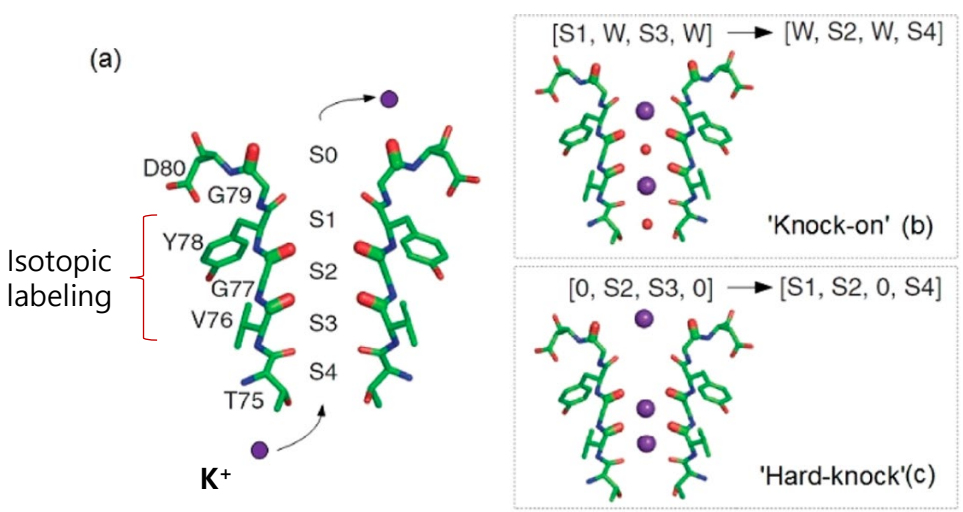


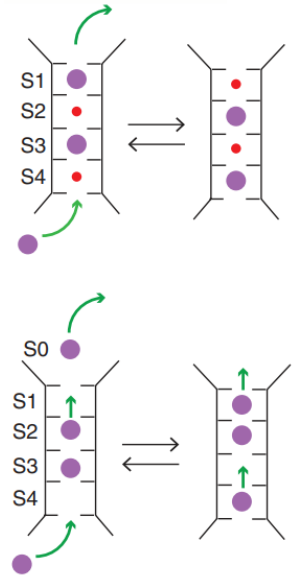
Experimental examples in the review article

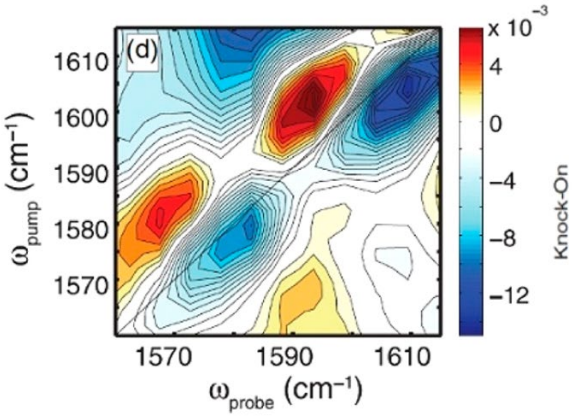
2D IR spectroscopy for ion permeation within trans-membrane bacterial channel protein KcsA

M. Zanni et al., **Science** (2016)

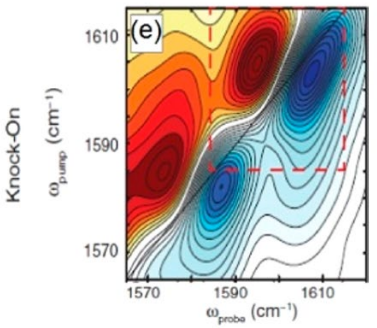




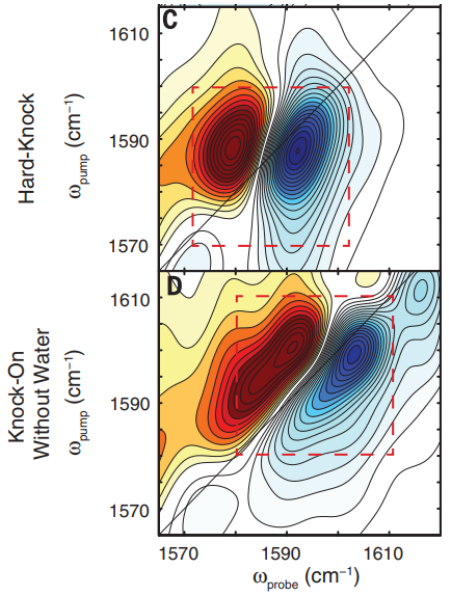




(labeled – unlabeled) spectrum

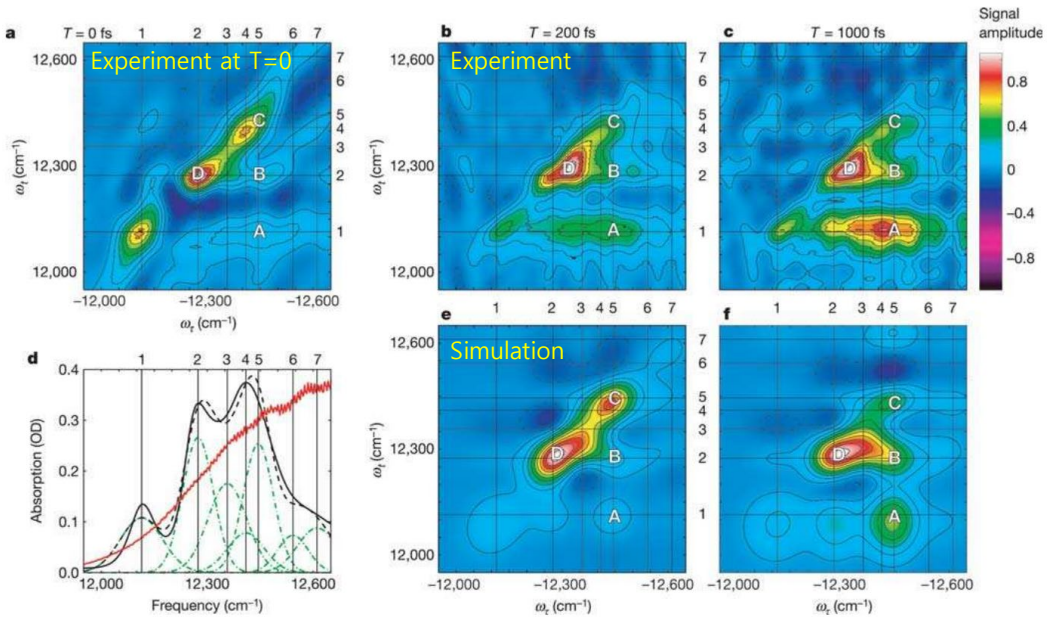


Simulation for 'Knock-on' model

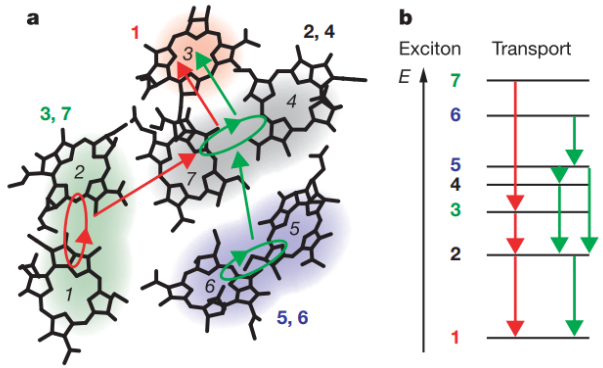


Experimental examples in the review article

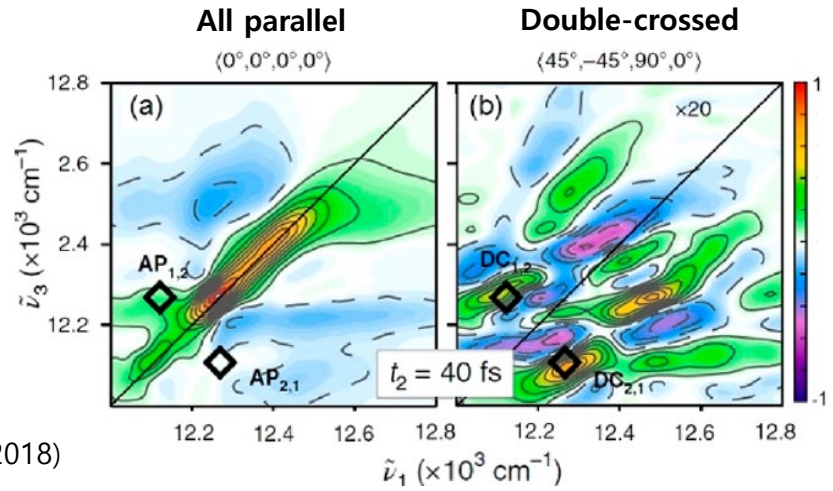
2D IR spectroscopy for photosynthetic process of FMO complex



T. Brixner et al., **Nature** (2005)



Bacteriochlorophylls (BChl) having 7 exciton states



E. Thyrhaug et al., **Nature Chem** (2018)