Ultrafast spectroscopy by sub-10fs pulse to study electronic and vibration dynamics

- real-time observation of molecular deformation during photo-isomerization

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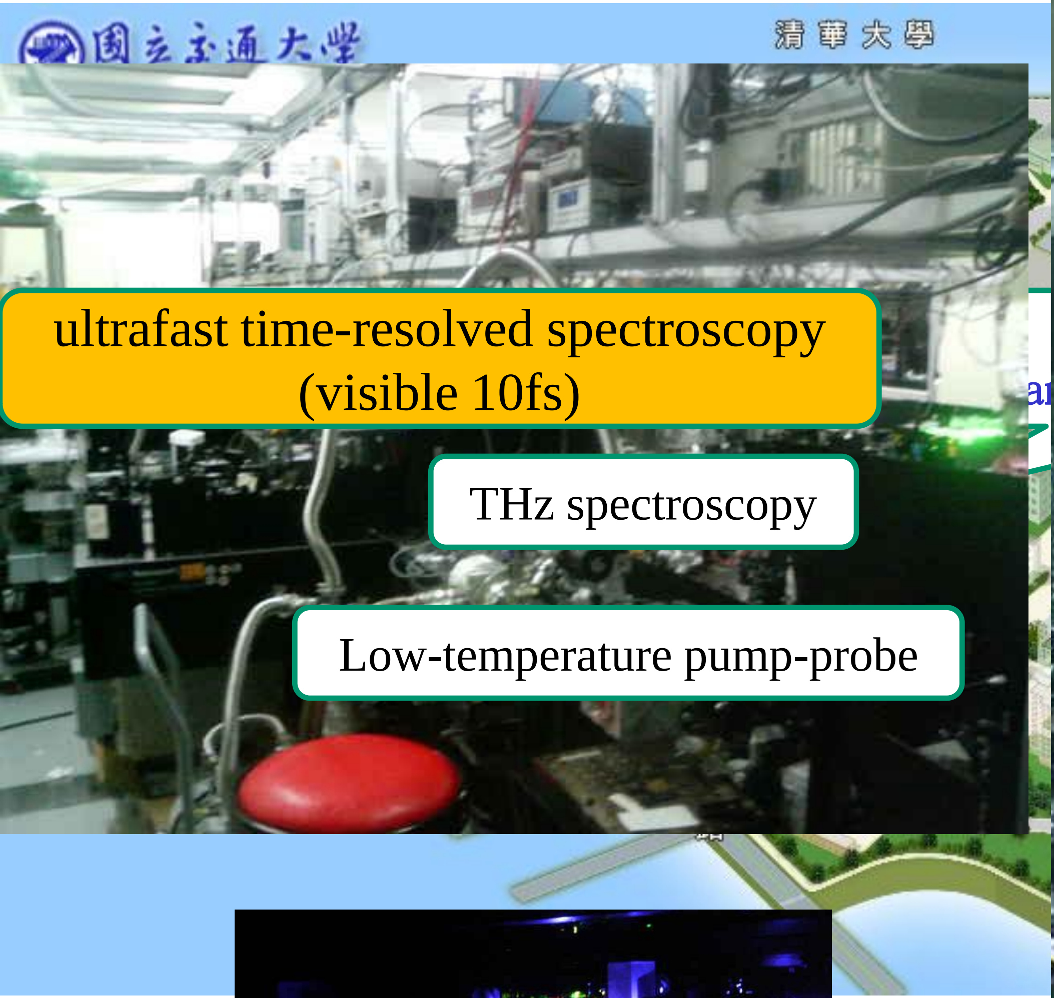
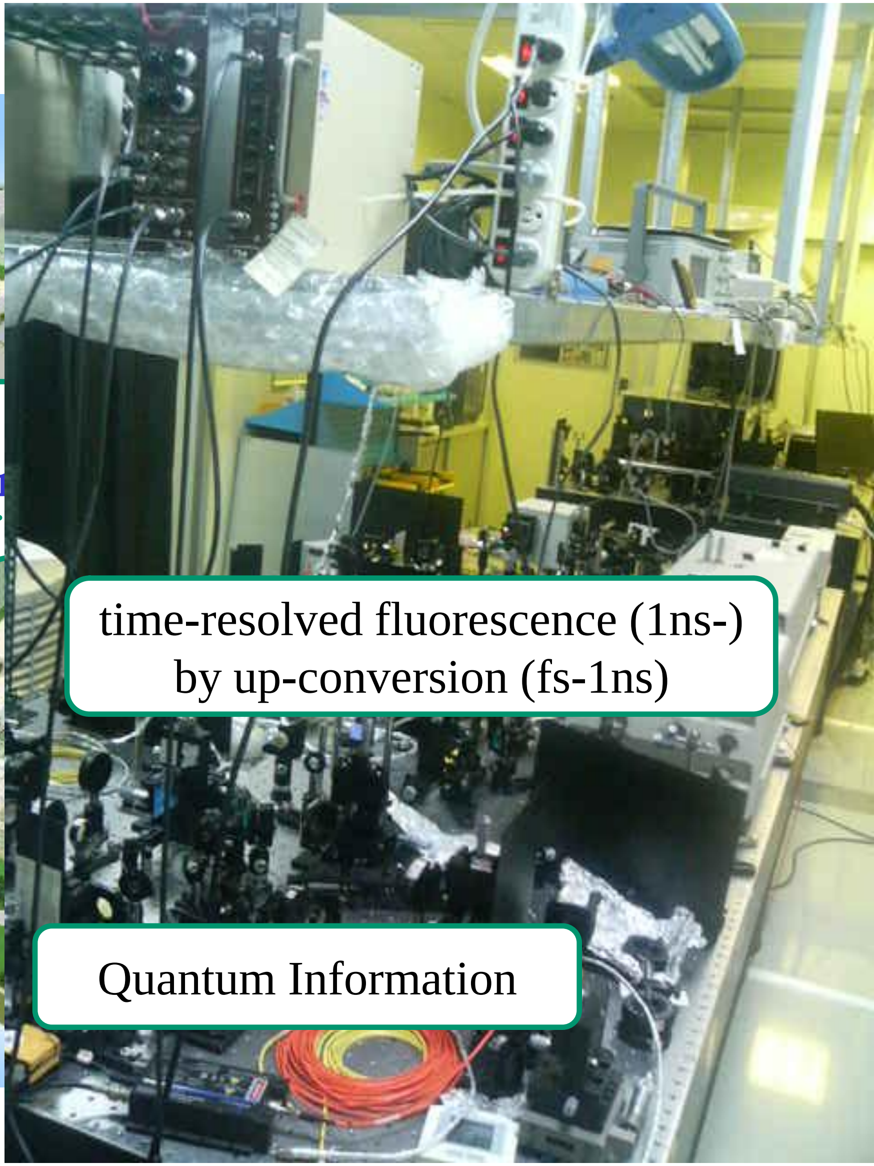

ultrafast time-resolved spectroscopy
(visible 10fs)
THz spectroscopy
Low-temperature pump-probe


time-resolved fluorescence (1ns-)
by up-conversion (fs-1ns)
Quantum Information

Outline

1 Introduction

- Ultrashort laser pulse (sub-10fs, visible)
- bacteriorhodopsin (bR)

2 Time-resolved absorption spectra (pump-probe)

3 Ultrafast dynamics of electronics states

4 Ultrafast dynamics of vibrational modes

- out-plane & in-plane modes (C=C-H bend)
- C=C bond length (C=C stretch)
- Wavepacket motion, Dynamics (C=C stretch)
- Vibrational phase (C=C stretch)

5 conclusion

1. Introduction

ultrashort laser pulse

1. Introduction (ultrashort laser pulse)

For the analysis of ultrafast dynamics,

ultrafast time resolution

$t<100$fs : time-resolved electronic states

$t<10$fs : time-resolved vibrational states

probe energy dependence of the dynamics

✓ broadband spectrum (ultrashort laser pulse)

✓ broadband detection system

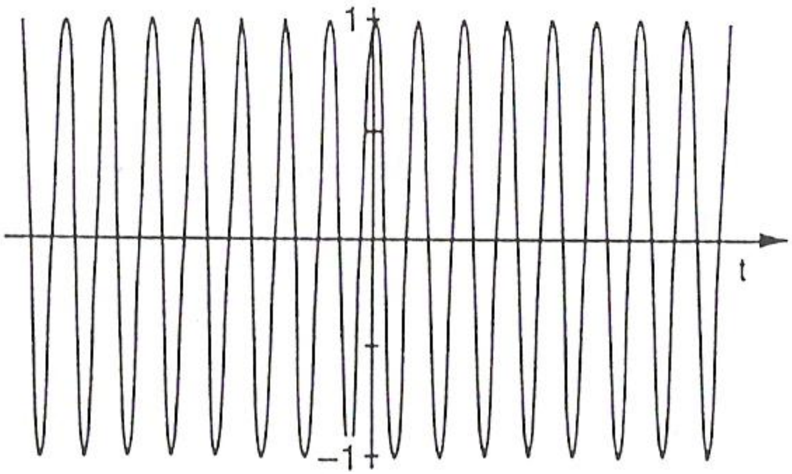
(CCD, multi-channel detectors)

how to generate ultrashort laser pulse ?

1. Introduction (ultrashort laser pulse)

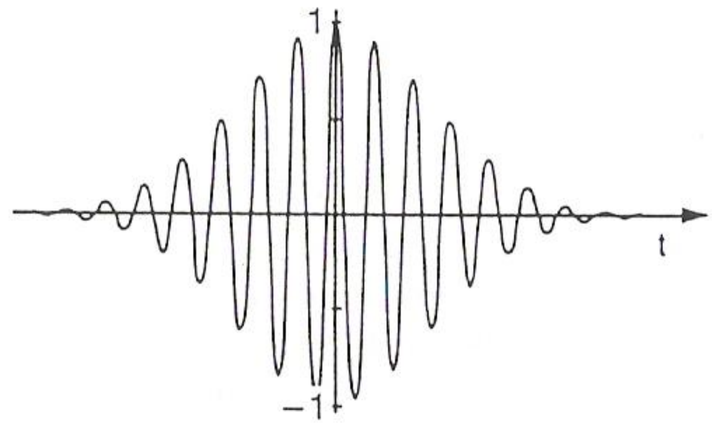
CW laser

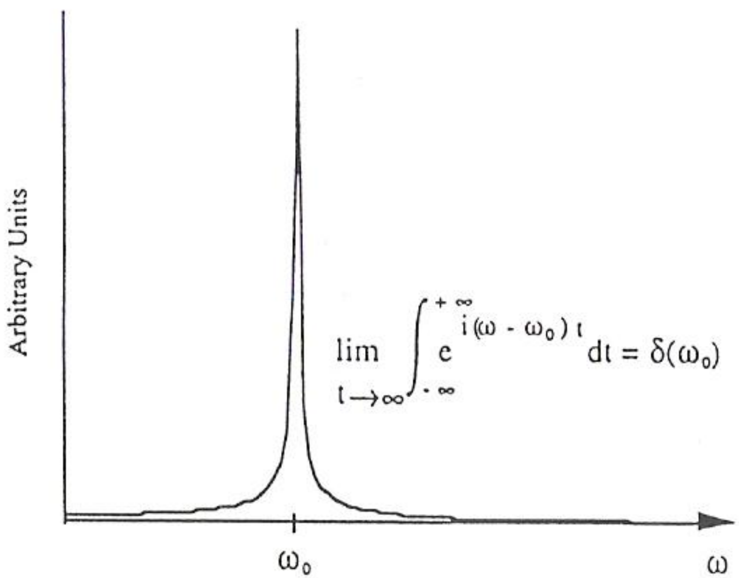
$$E_y = \mathrm{Re}\left(E_0\, \mathrm{e}^{\mathrm{i}\omega_0 t}\right)$$

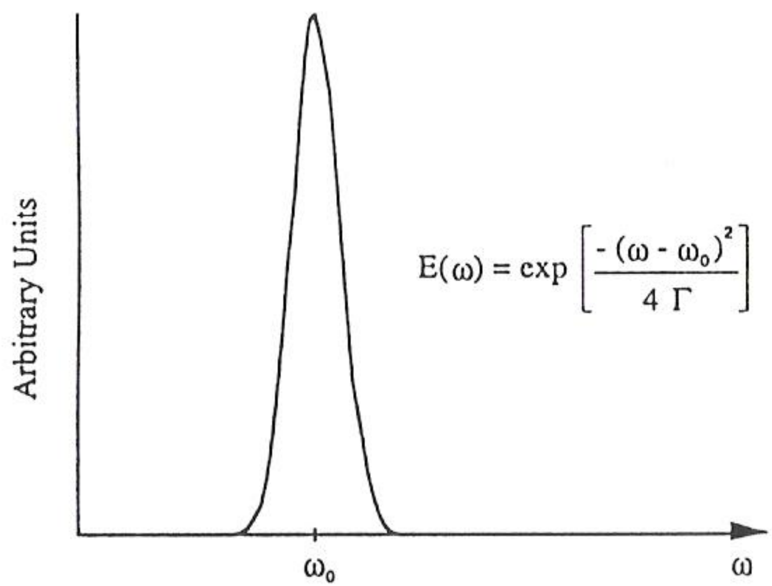


pulse laser

$$E_y = \mathrm{Re}\left(E_0\, \mathrm{e}^{(-\Gamma t^2 + \mathrm{i}\omega_0 t)}\right) \qquad \Gamma \propto t_0^{-2}$$

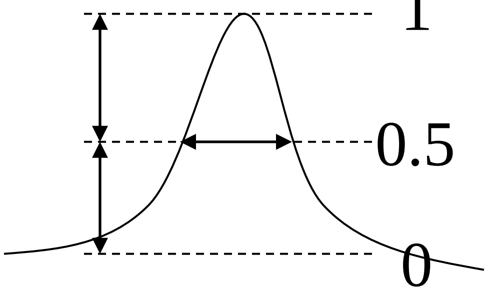






1. Introduction (ultrashort laser pulse)

useful measure : FWHM (full width half maximum)



$$\Delta\nu \cdot \Delta t \geq K/2$$

Shape	$\varepsilon(t)$	K
Gaussian function	$\exp[-(t/t_0)^2/2]$	0.441
Exponential function	$\exp[-(t/t_0)/2]$	0.140
Hyperbolic secant	$1/\cosh(t/t_0)$	0.315
Rectangle	–	0.892
Cardinal sine	$\sin^2(t/t_0)/(t/t_0)^2$	0.336
Lorentzian function	$[1+(t/t_0)^2]^{-1}$	0.142

For ultrashort laser pulse,

<u>broadband spectrum generation</u> is needed

Solid-State Lasers

substitute solids for gases and dyes as gain media

increase generated power density, easy operation

The neodymium Ion (Nd^{3+})

1% doped in YAG, YAP, YLF, phosphate glass…

1.06μm emission (SHG~532nm)

broad band (than gas) : surrounding solid matrix

typical CW pumped, active mode-locked

(100ps, 80MHz, 1.06μm, several Watts)

ex.) 532nm=light source for synchronously pumped sub-ps dye laser

larger intensity = more modes = shorter pulse

Gain increase by Q-switching

1ps in Nd:YAG/YLF/YAP

sub-ps in Nd:glass

The Titanium Ion (Ti3+)

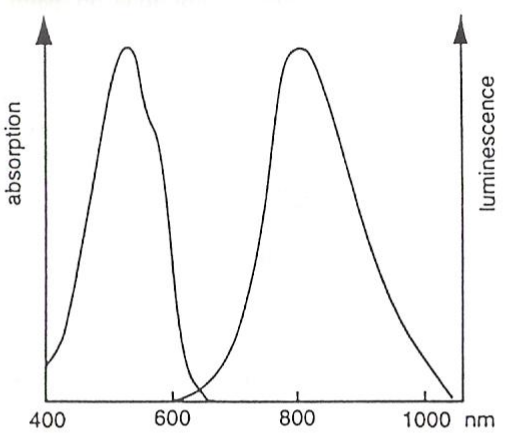
0.1% wt. in aluminum oxide (Ti:Al_2O_3, Ti:sapphire)

$\phi(Ti^{3+}) = \phi(Al^{3+})*1.26$: strong distortion cause unusual broadband

absorption : ground (^2T_g)
to excited (^2E_g, two sub levels separated by 50nm)

^2T_g,^2E_g are strongly coupled to vibrational modes

(strong homogeneous broadening)



red-shifted emission (200nm width @ 750nm)

high thermal conductivity (~metals) at low temp.
(ex. CW optical pump can be ~20W)

mode lock : active, passive (dye jet, colored glass), self (KLM)

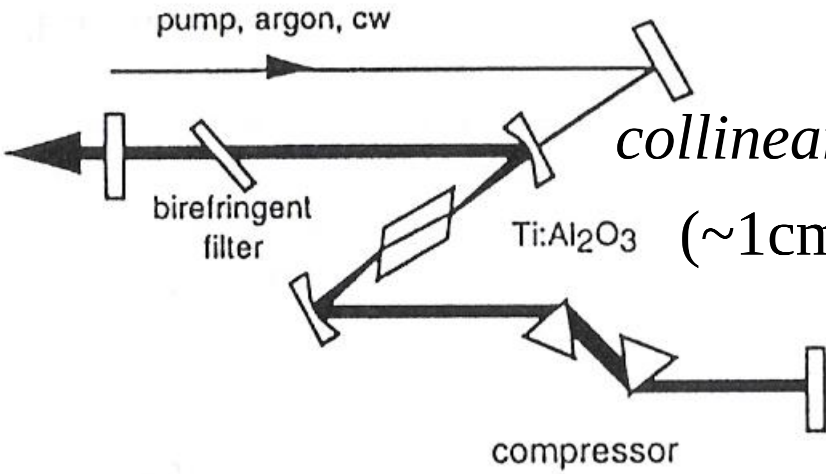
KLM starts with intensity fluctuation

synchronous pump, moving mirror (not stable)

external cavity with nonlinear optical elements (stable)

<u>typical setup for Ti:sapphire laser</u>

all-line blue-green Ar laser (10W, CW)



collinear pump

(~1cm)

nowadays ~10fs is available

100fs, 80MHz, ~1W (commercial)

peak power ~100kW directly

nonlinear phenomena observation without amplification

Self-Phase-Modulation (SPM) –time dependent-

$$n = n_0 + \frac{1}{2} n_2 I(t) \ , \qquad \text{with} \ \ I(t) = \mathrm{e}^{-\Gamma t^2}$$

assuming plane wave

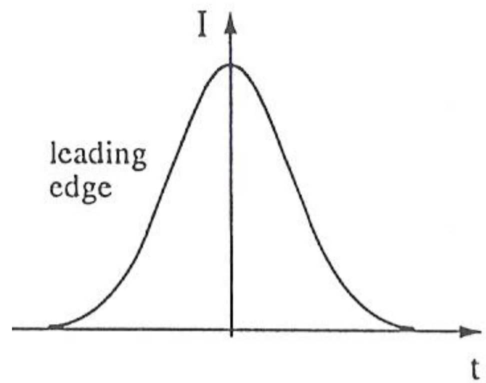
$$E(t,x) = E_0 \, \mathrm{e}^{\mathrm{i}(\omega_0 t - kx)} \ , \qquad k = \frac{\omega_0}{c} n(t)$$

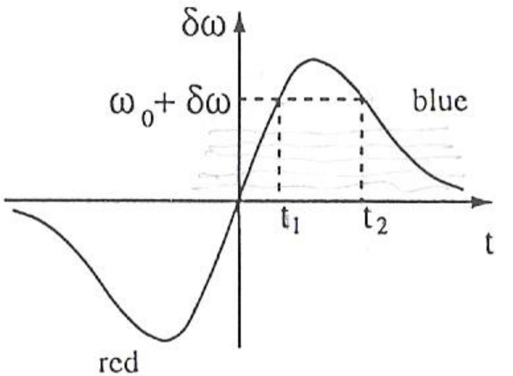
instantaneous frequency

$$\omega(t) = \frac{\partial}{\partial t} \Phi(t) = \omega_0 - \frac{\omega_0}{c} \frac{\partial n(t)}{\partial t} x$$

frequency variation

$$\delta\omega(t) = \omega(t) - \omega_0 = -\frac{\omega_0 n_2}{2c} x \frac{\partial I(t)}{\partial t}$$





It means…

leading edge : *low frequency (long wavelength)*

trailing edge : *high frequency (short wavelength)*

note : <u>they are created inside the original pulse envelope</u>

(pulse width does not change by SPM)

not transform-limited, may be stretched because of chirp…

1. Introduction (ultrashort laser pulse)

For ultrashort laser pulse,

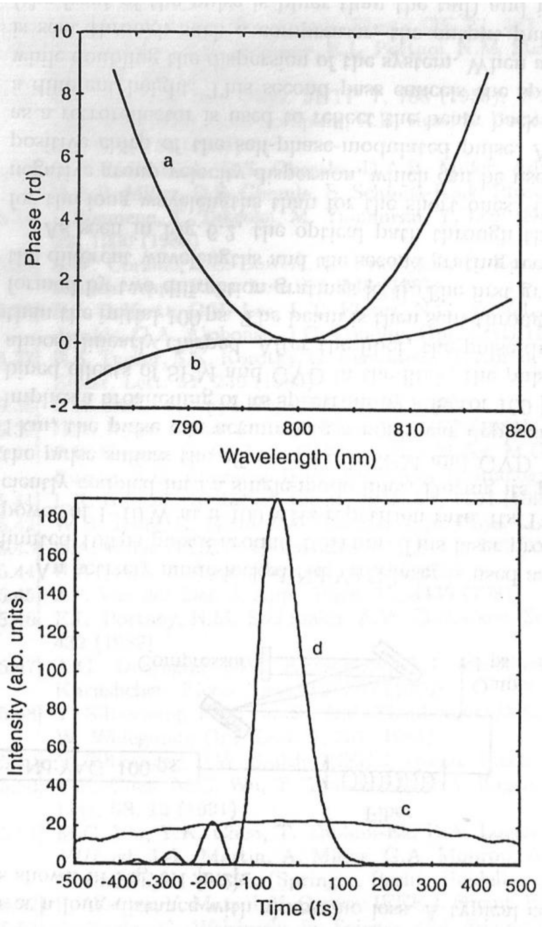
broadband visible spectrum obtained (SPM)

broadband laser pulse is easily **broadened**

because of material **chirp**

red light runs faster

blue light runs slower



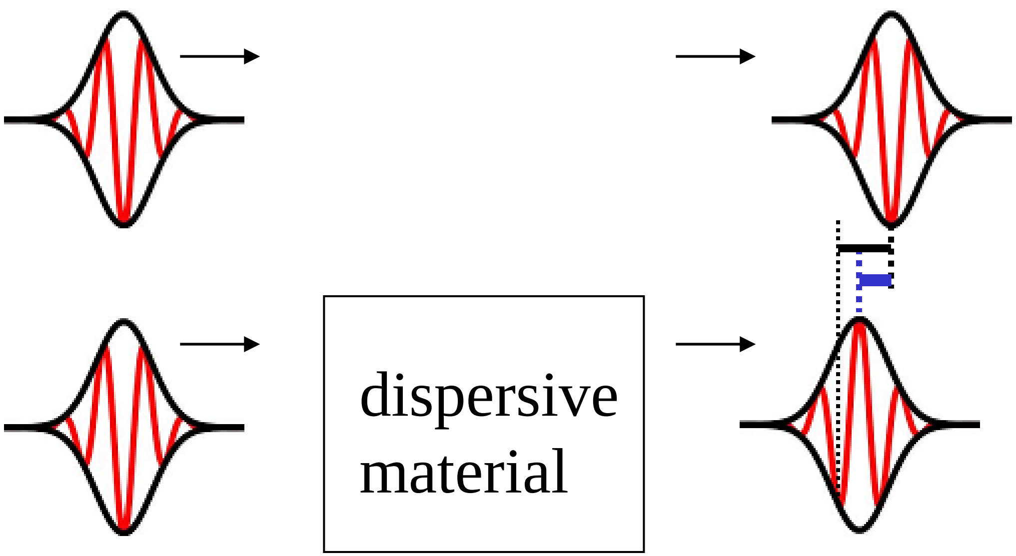
1. *Introduction (ultrashort laser pulse)*

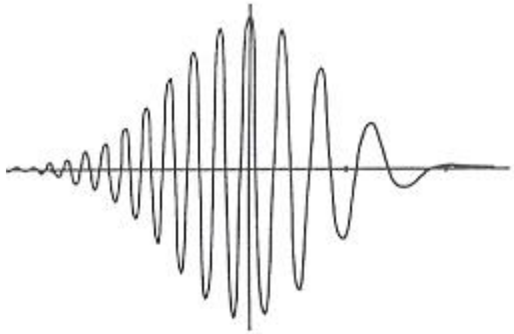
Propagation of a Light Pulse in a Transparent Medium

$$\varepsilon(t,x)=\sqrt{\frac{\Gamma(x)}{\pi}}\exp\left[\mathrm{i}\omega_0\left(t-\frac{x}{v_\phi(\omega_0)}\right)\right]\exp\left[-\Gamma(x)\left(t-\frac{x}{v_\mathrm{g}(\omega_0)}\right)^2\right]$$

$$v_\phi(\omega_0)=\left(\frac{\omega}{k}\right)_{\omega_0}\quad,\qquad v_\mathrm{g}(\omega_0)=\left(\frac{\mathrm{d}\omega}{\mathrm{d}k}\right)_{\omega_0}\quad,$$

phase delay group delay

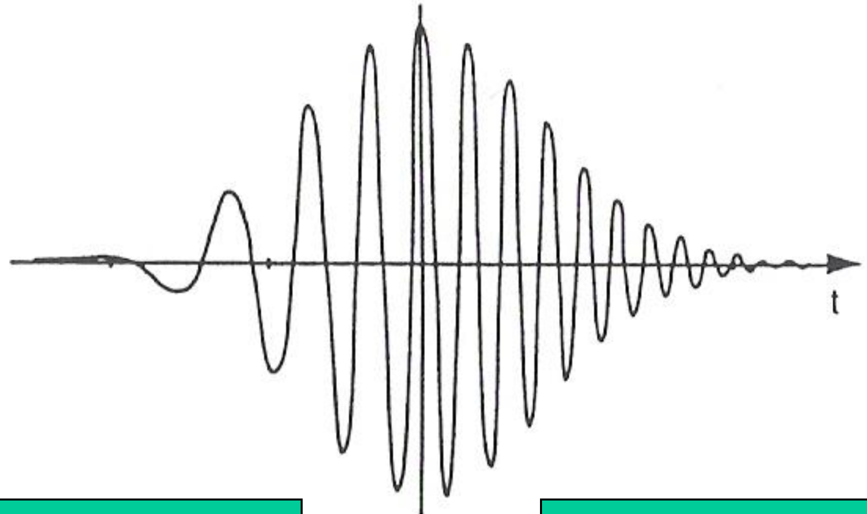




called as "positive chirp"

1. Introduction (ultrashort laser pulse)

$\omega(t) = \partial\Phi/\partial t$: **instantaneous angular frequency**



transform limited (TL)

$$\omega(t) = \partial\Phi/\partial t = \omega_0$$

$$E_y = \mathrm{Re}\left(E_0\, \mathrm{e}^{(-\Gamma t^2 + \mathrm{i}\omega_0 t)}\right)$$

chirped pulse :

$$\omega(t) = \partial\Phi/\partial t = \omega_0 + \alpha t$$

$$E_y = \mathrm{Re}\left(E_0\, \mathrm{e}^{[-\Gamma t^2 + \mathrm{i}(\omega_0 t - a t^2)]}\right)$$

For ultrashort pulse

Chirped pulse should be compressed

1. Introduction (ultrashort laser pulse)

for the pulse compression

- grating compressor
  - different color diffracted in different angle
- prism compressor
  - different color refracted in different angle
- chirp mirror
  - different color reflected in different layer

grating compressor

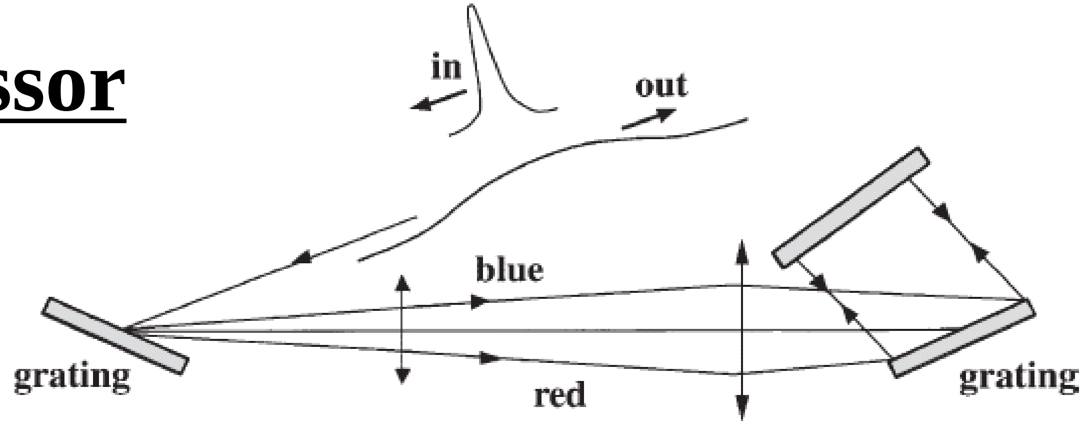
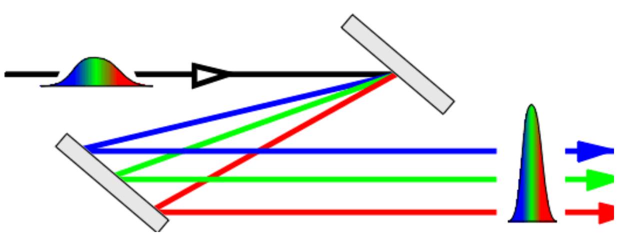
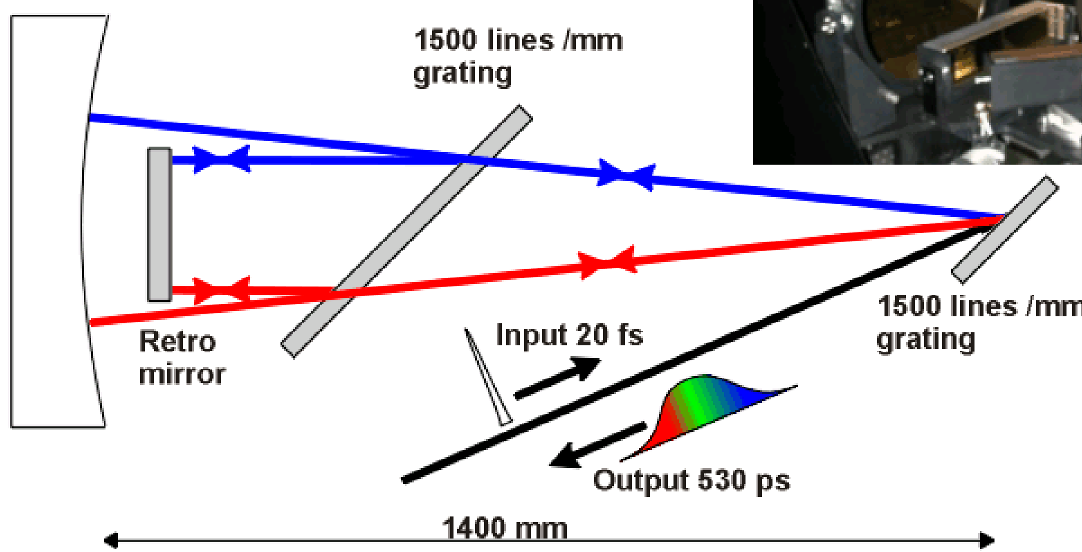
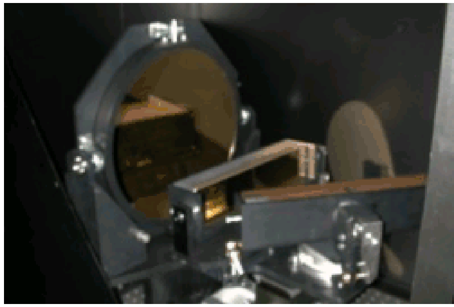


Fig. 6.8. Typical stretcher setup. The lenses located between the two gratings can be replaced by mirrors to reduce the chromatic aberrations







1. Introduction (ultrashort laser pulse)

GVD (group velocity dispersion)

spectral dephasing (keeps spectral amplitude)

SPM (Self-Phase Modulation)

temporal dephasing (keeps temporal profile)

red-shift in pulse front and blue-shift in tail

compress with dispersion

reduce TL-pulse width : **both of SPM and GVD**

nonlinear waveguide (SM fiber etc…)

long distance accumulation w/o loss

uniform spectral broad

(generally small broadening on edge)

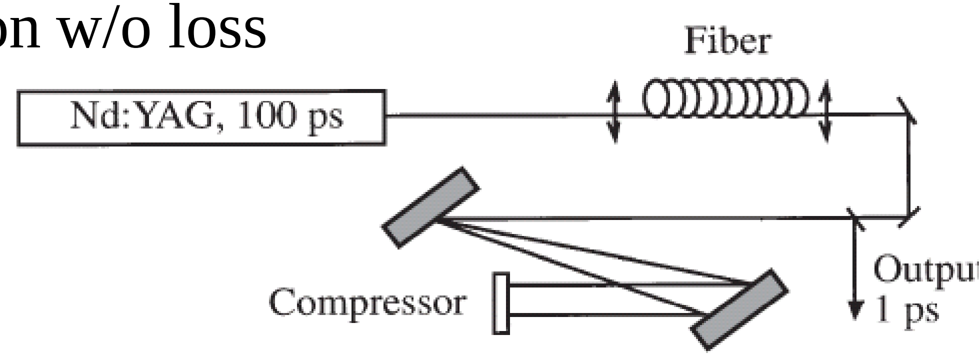
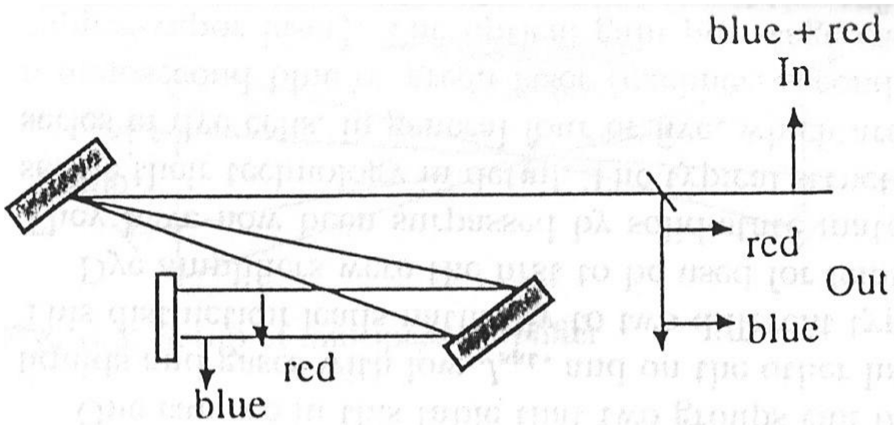


Fig. 6.1. Typical setup for pulse compression

active ML Nd:YAG laser

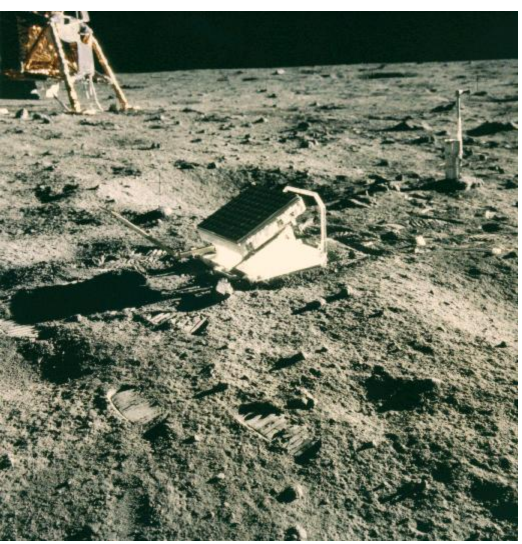
: 100ps TL, 1064nm, 1-10W, 100MHz, TEM_{00} to SM fiber (~1km)

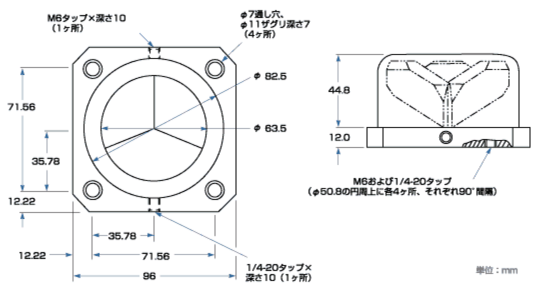
SPM : dephasing of 200π, broadening by a factor 100

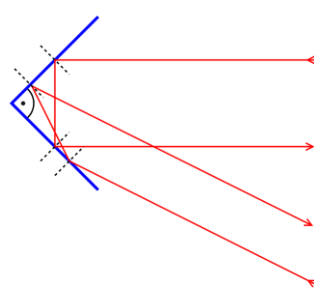


Red is longer (negative chirp)

cf.) SPM (positive chirp)







retro-reflector (corner-reflector)

…to shift the beam

grating compressor

for rough compression

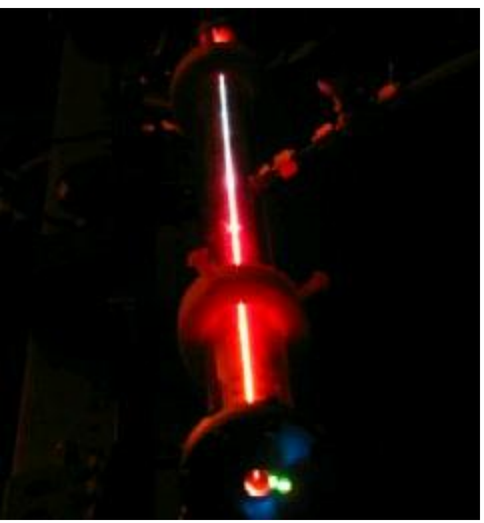
(or generate negative chirp)

100ps-positive(?) chirped pulse (a,c)

1ps-compressed as (b,d)

autocorrelation trace is shown

spectral amplitude keeps same



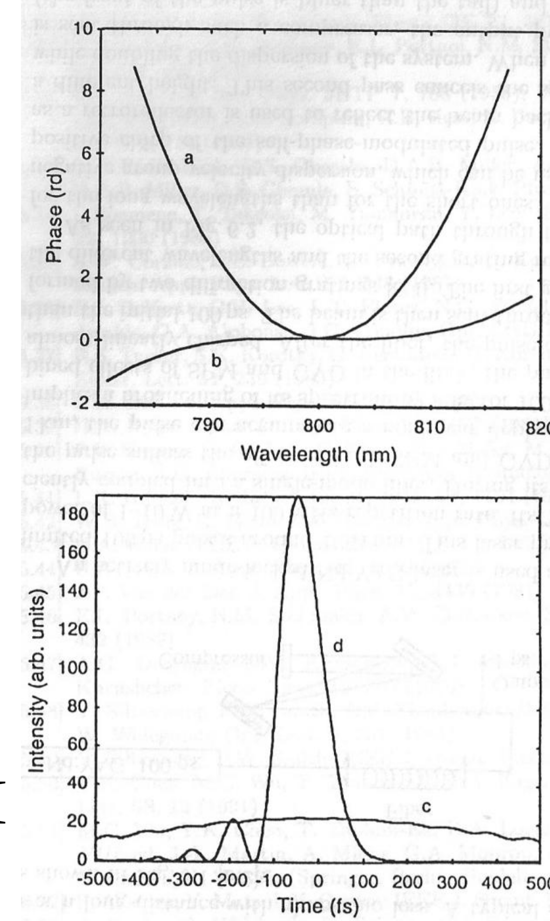
hollow glass waveguide for SPM

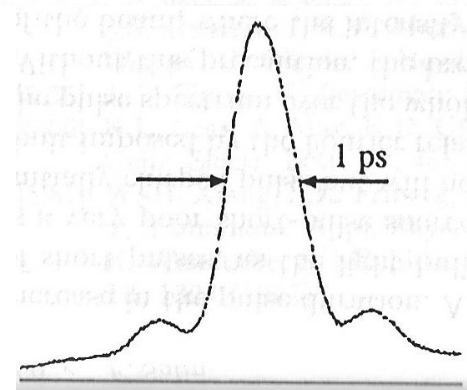
filled with noble gas (Xe…)

can avoid damage

used for ultra-short pulse

(high peak power)





prism compressor

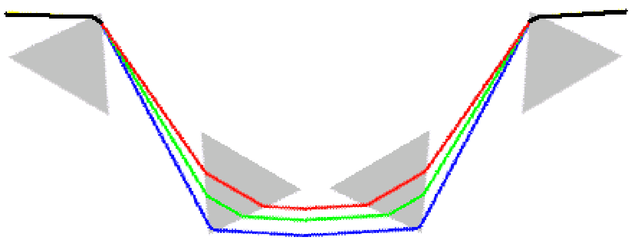
1. first prism introduce ***angular dispersion*** : n(λ) depends on λ

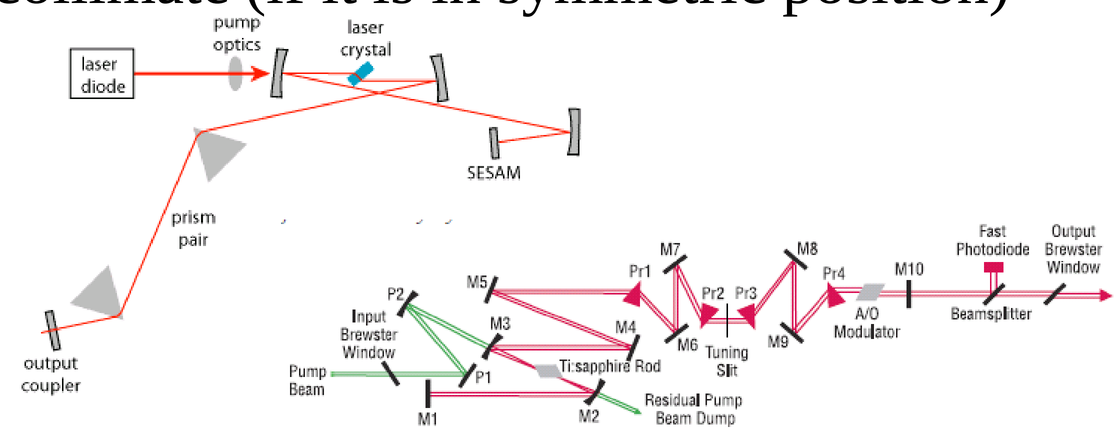
2. collimated by another prism in special angle

    frequency components spread across the diameter

    (***spatial dispersion)***

3. another prism pair re-collimate (if it is in symmetric position)





good points

small loss (useful for laser cavity)

bad points

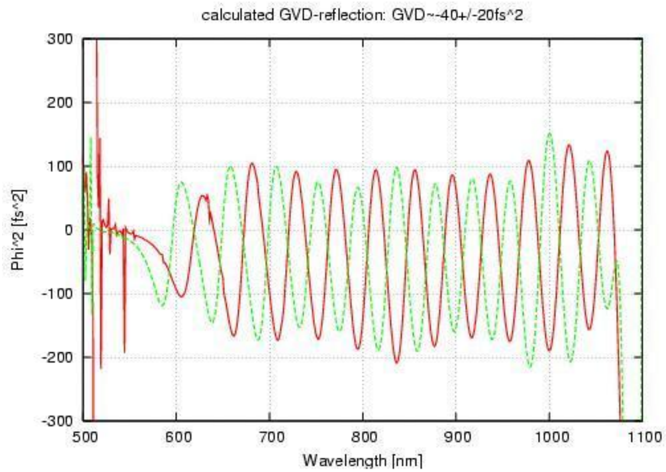
need long separation between the prisms for negative GVD

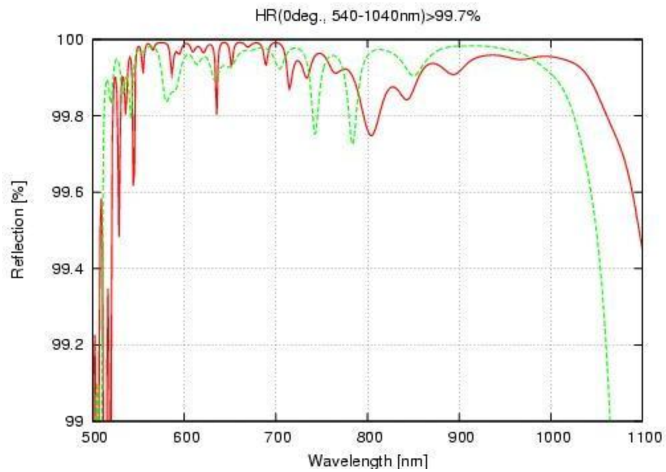
Chirp mirror

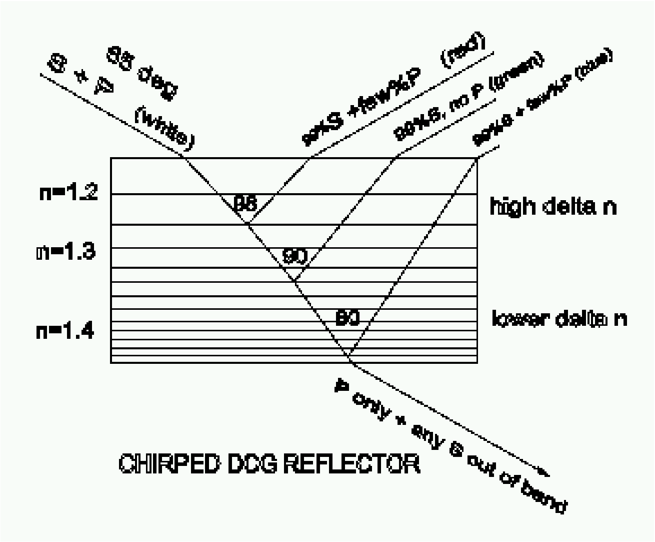
multilayered dielectric dispersion

positive — not for broadband

negative — useful for compression

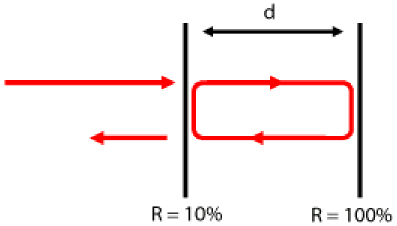


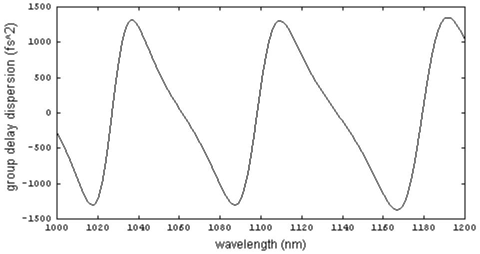




spectral narrowing increase duration

Gires-Tournois interferometer





<u>*1. Introduction (ultrashort laser pulse)*</u>

For ultrashort laser pulse,

<u>broadband visible spectrum</u> obtained (SPM)

<u>pulse compression</u> (grating compressor)

but last problem remains

signal intensity of SPM is ***<u>too weak</u>***

amplification of the signal is needed

dye, solid-material, ...

for certain wavelength

optical parametric amplifier (**OPA**)

tunable (narrow band)

non-collinear OPA (**NOPA**)

tunable (broad band)

Amplification

assume "excited-state lifetime of amp medium" >> other processes

small-signal gain : $g_0 = J_{sto}/J_{sat}$

J_{sto} : energy stored in medium
J_{sat} : saturated influence (J/cm^2)

$$J_{sat} = \frac{hv}{\sigma_e}$$

σ_e : gain cross section
v : freq. of transition

saturation intensity

$$I_{sat} = \frac{J_{sat}}{\tau_f}$$

τ_f : fluorescence lifetime of laser medium

$$J_{sto} = \frac{E_p \alpha}{S} \frac{\lambda_p}{\lambda_L}$$

E_p : pump energy
α : absorption of pump
S : cross-section of pump beam
λ_p, λ_L : λ of pump, laser
(experimental values)

absorbed fluence E_p/S

λ_p/λ_L called the quantum defect.

Amplification

$E_{out}=E_{in}\exp(g_0)$: E_{in} is amplified (@ low E_{in})

output fluence @ high E_{in} (*Frantz and Nodvick*)

$$J_{out} = \frac{E_{out}}{S} = J_{sat} \ln\left\{g_0\left[\exp\left(\frac{J_{in}}{J_{sat}}\right) - 1\right] + 1\right\}$$

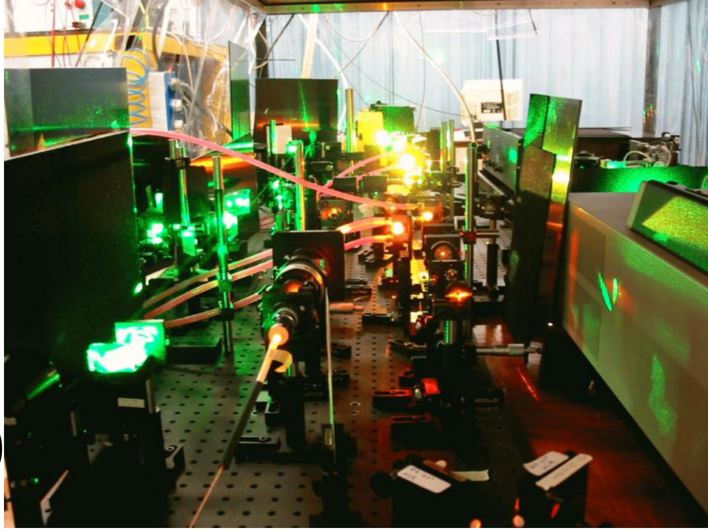
saturation fluences

Amplifier medium	J_{sat}	Spectral range
Dyes	$\sim 1\,mJ/cm^2$	Visible range
Excimers	$\sim 1\,mJ/cm^2$	UV range
Nd:YAG	$0.5\,J/cm^2$	At $\approx 1064\,nm$
$Ti{:}Al_2O_3$	$1\,J/cm^2$	At 800 nm
Cr:LiSAF	$5\,J/cm^2$	At 830 nm
Nd:glass	$5\,J/cm^2$	At $\approx 1054\,nm$
Alexandrite	$22\,J/cm^2$	At $\approx 750\,nm$

liquid, gas : low J_{sat}

solid : high J_{sat}

Dye amplifier (liquid)



4 or 5 dye cells

transversely pumped by ns-blue/green laser

(excimer, SH of Nd:YAG, Cu-vapor laser)

high optical gain (~10^3/per stage, 10^6/4 steps)

5-10% of ASE (ns-broad pedestal)

even with saturable absorber/spatial filtering

pump efficiency of SH of Nd:YAG (0.1-0.3%)

Excimer amplifier (gas)

still used for high power UV (large amp diameter)

low J_{sat} as dye *advantages* (high optical gain)

drawbacks (ASE)

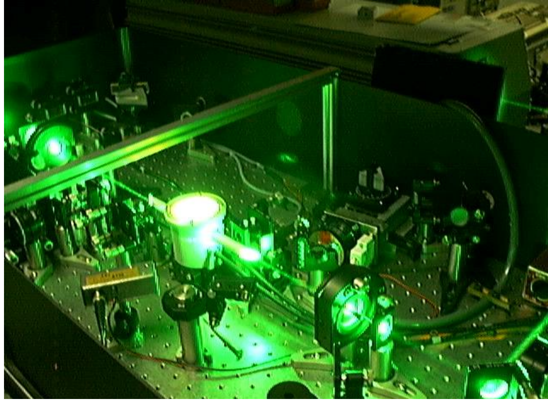
Solid amplifiers

high J_{sat}…low optical gain per pass

multipass amplification

regenerative amplification

Multipass amplification



bow-tie (each pass separated geometrically)
#pass (4 or 8) limited by geometry
for higher gain : cascaded
    long pass
    close to damage threshold
only technique for >50mJ

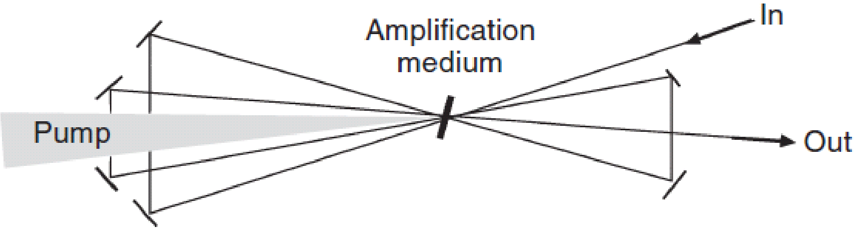
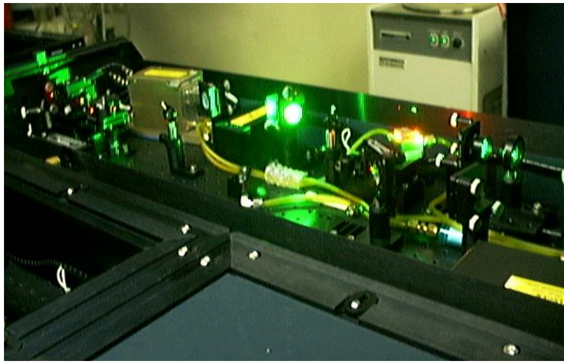


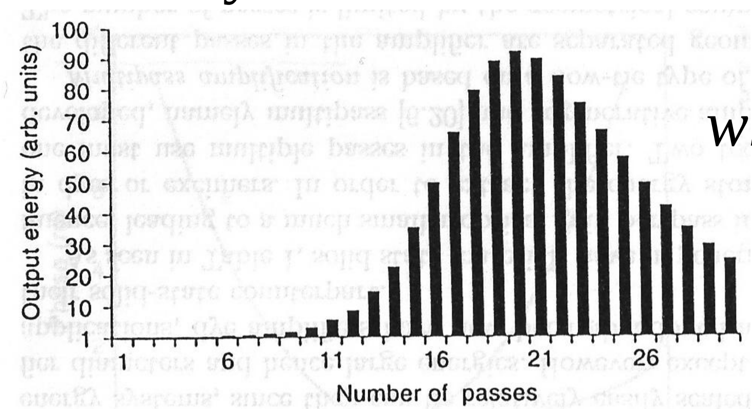
Fig. 6.5. Setup of multipass amplifier

Regenerative amplification



pulse trapped in a laser resonator
by Pockels cell and a broadband polarizer

why decrease after 20 ?



simulation : *Franz-Nodvick model*

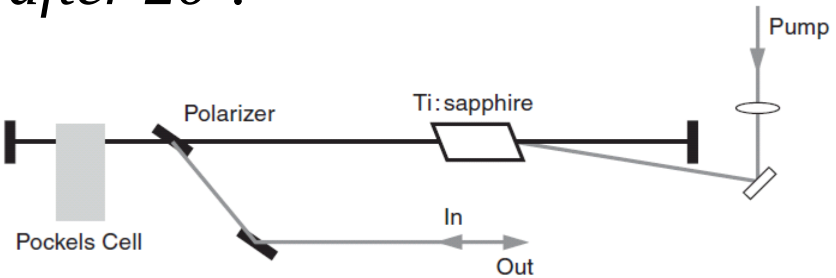
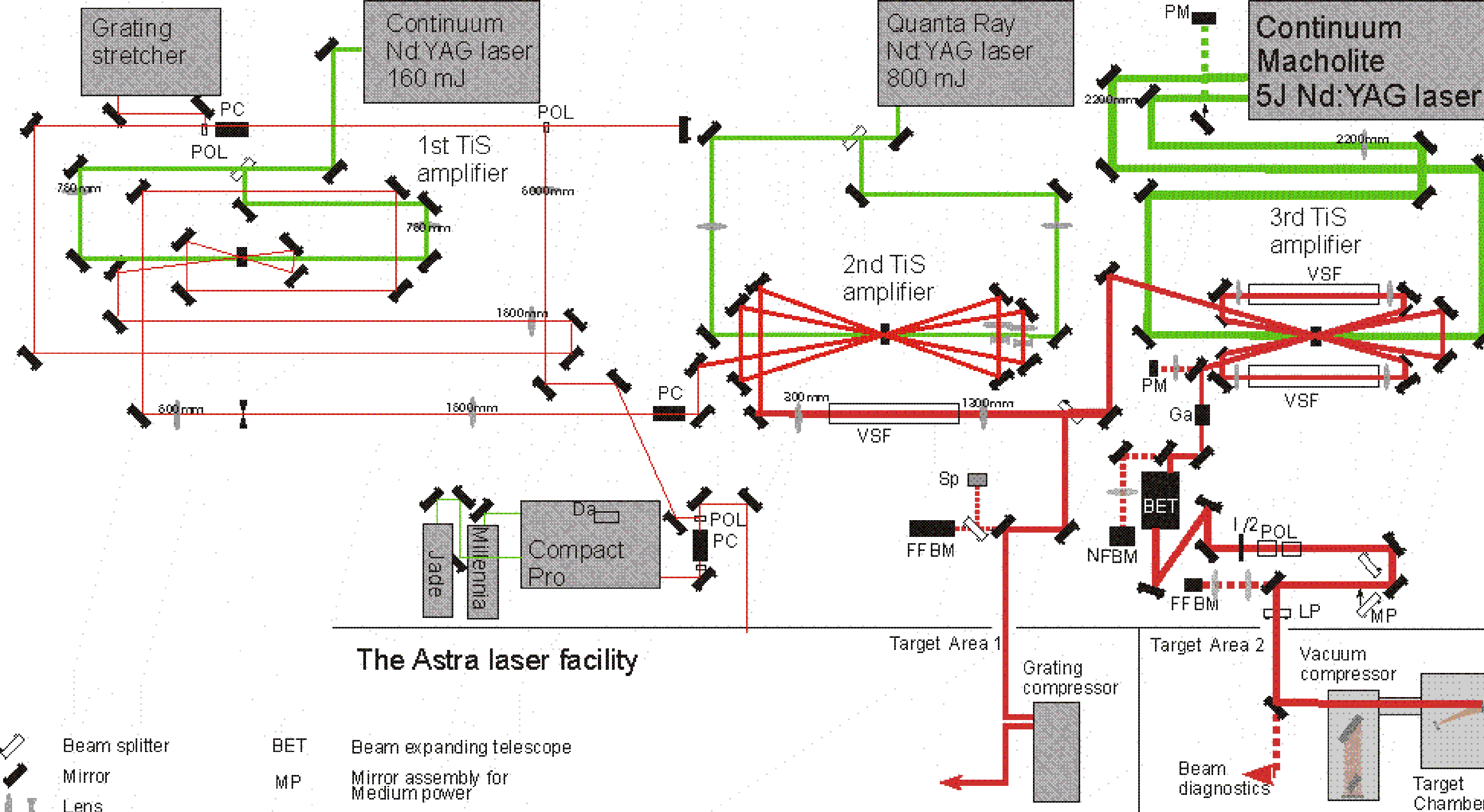


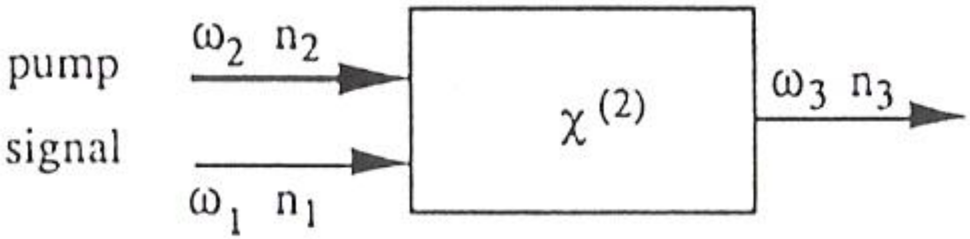
Fig. 6.6. Setup of regenerative amplifier



	Beam splitter	BET	Beam expanding telescope
	Mirror	MP	Mirror assembly for Medium power
	Lens		
Sp	Spectrometer		
F	Faraday isolator	NFBM	Near field beam monitor
	Pin hole	FFBM	Far field beam monitor
PC	Pockels cell	l /2	Variable attenuator
Ga	Galvo	Da	Dazzler
PM	Power meter	VSF	Vacuum spatial filter
CT	Collimating telescope	POL	Polariser
		LP	Mirror Assembly for Low power

- Ti:sapphire (Ti:Al_2O_3) 650–1100 nm
- alexandrite (Cr:Be_2O_3) 700–820 nm
- colquirites (Cr:LiSAF, Cr:LiCAF, etc.) 800–1000 nm
- Fosterite 1250–1300 nm
- Yb doped materials 1030–1080 nm
- glasses (Nd:glass) 1040–1070 nm.

Parametric Interaction



energy conservation
momentum conservation

Photon number variation	$\omega_1 > \omega_2$	$\omega_1 < \omega_2$	Photon number variation
$n_1 - 1$ $n_2 + 1$ $n_3 + 1$	Frequency difference $\omega_3 = \omega_1 - \omega_2$ $k_1 = k_2 + k_3$	Frequency sum $\omega_3 = \omega_2 + \omega_1$ $k_3 = k_1 + k_2$	$n_1 - 1$ $n_2 - 1$ $n_3 + 1$
$n_1 - 1$ $n_2 - 1$ $n_3 + 1$	Frequency sum $\omega_3 = \omega_1 + \omega_2$ $k_3 = k_1 + k_2$	Parametric amplification $\omega_3 = \omega_2 - \omega_1$ $k_2 = k_1 + k_3$	$n_1 + 1$ $n_2 - 1$ $n_3 + 1$

Optical Parametric Amp. (OPA)

semi-classical (field is quantized) : virtual electronic transitions

particular direction (phase matching)

$$\omega_3 = \omega_2 - \omega_1, k_3 = k_2 - k_1$$

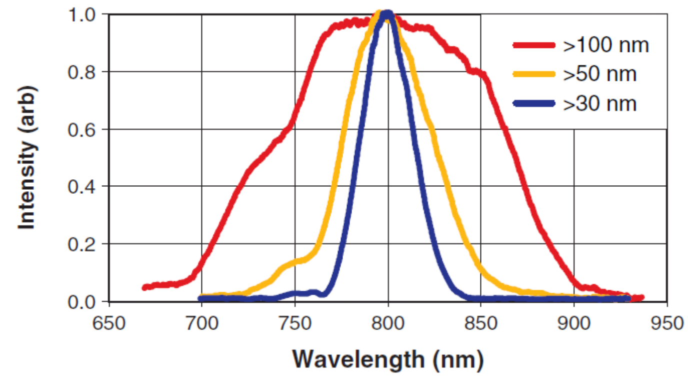
cf.) Spontaneous Fluorescence **(Opt. Param. Generation : OPG)**

start with ambient noise ($\omega_1 < \omega_2$)

Wavelength Conversion

Ti:S laser : ~800nm

only tunable around NIR



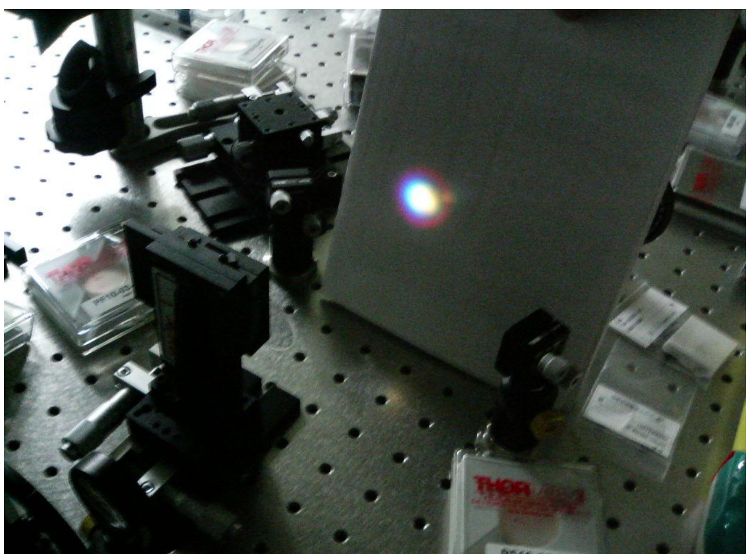
focus high energy (>10^{13}W/cm^2)…self-focusing and SPM

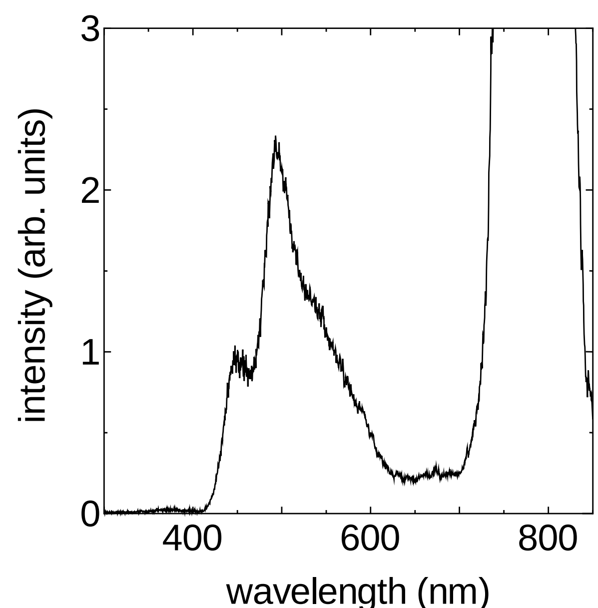
small filaments emit white light (200-1500nm)

small intensity in λ <<800nm or λ>>800nm

can be used only for probe pulse (not for pump or trigger)

for wide tuning and strong power…parametric process





Parametric device :

nonlinear quadratic crystal (large $\chi^{(2)}$)

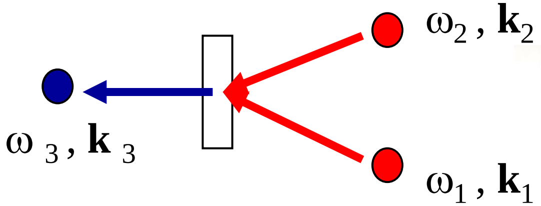
BBO (β-BaB_2O_4)

LBO($Li_2B_4O_7$)

KTP ($KTiOPO_4$), etc…

$\omega_3=\omega_1+\omega_2$ or $\omega_3=|\omega_1-\omega_2|$

$\mathbf{k}_3=\mathbf{k}_1+\mathbf{k}_2$ ($\mathbf{k}_j$: wave vector)

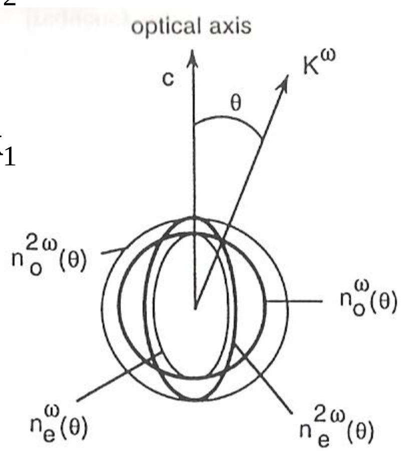


$$n_3\omega_3 = n_1\omega_1 + n_2\omega_2$$

(n(λ), generally not fulfilled)

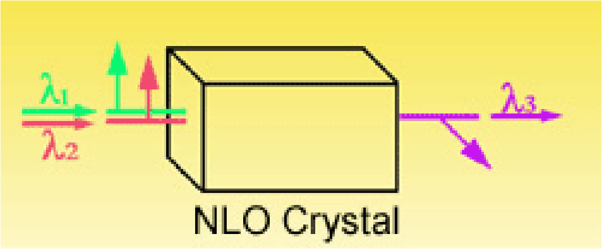
birefringence of the crystal

$n_e(\lambda,\theta)\neq n_o$…phase match angle

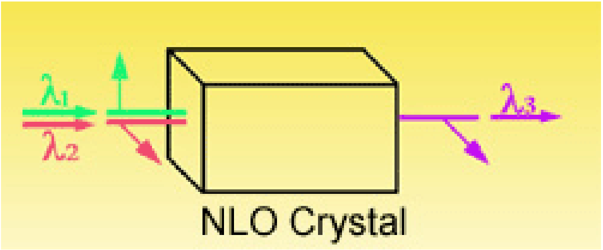


(ref. chap2)

type-I



type-II



For short pulse generation in parametric process (broad phase match)

phase match : $\omega_3=\omega_1+\omega_2$ or $\omega_3=|\omega_1-\omega_2|$

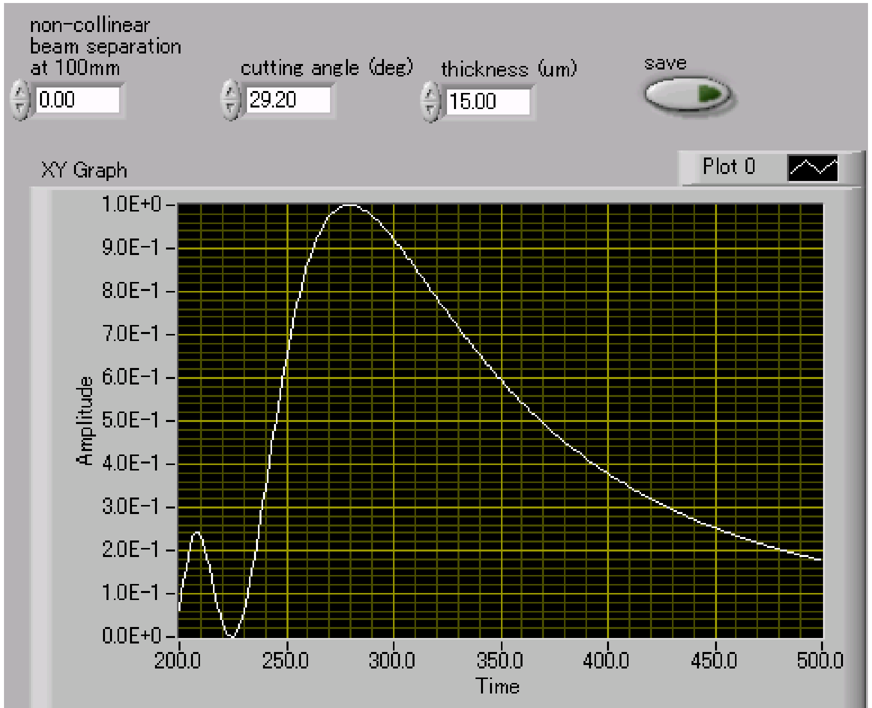
$\mathbf{k_3}=\mathbf{k_1}+\mathbf{k_2}$ ($\mathbf{k_j}$: wave vector)

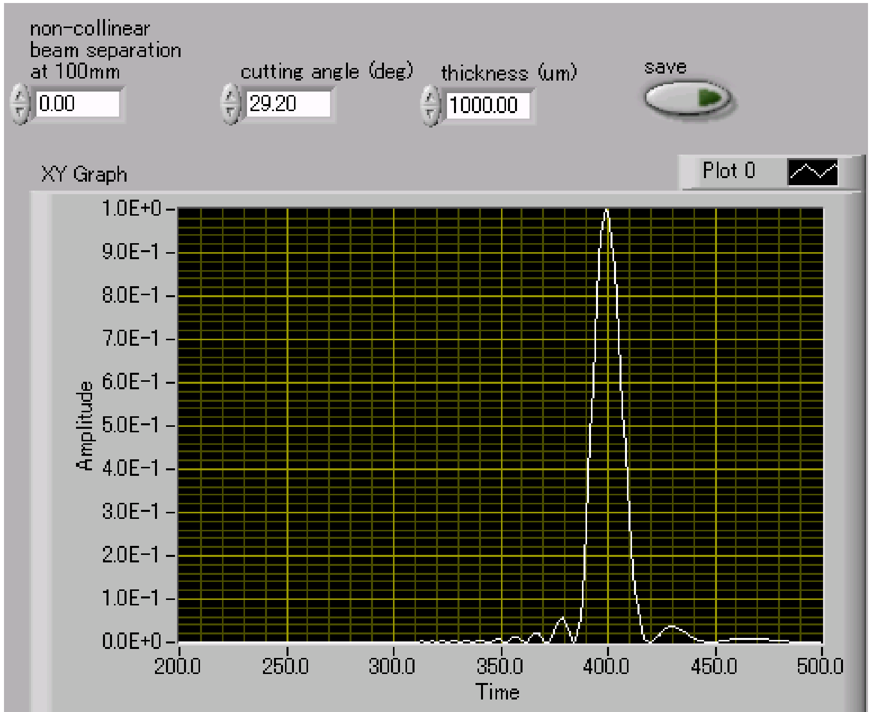
broadband phase match = GVD match ($v_g=dk/d\omega$)

thin crystal

broadband phase match

small GVD (keep high peak pow. / high conversion eff.)





A. Baltuska, M.S. Phenichnikov, D.A. Wiersma, Second-Harmonic Generation Frequency-Resolved Optical Gating in the Single-Cycle Regime, *IEEE J. Quant. Elect.* 35, 459 (1999)

detector sensitivity, and an ideal FROG signal $S^{\mathrm{SHG}}_{\mathrm{FROG}}(\Omega, \tau)$

$$S(\Omega, \tau, L) \propto R(\Omega) S^{\mathrm{SHG}}_{\mathrm{FROG}}(\Omega, \tau) \tag{31}$$

where

$$S^{\mathrm{SHG}}_{\mathrm{FROG}}(\Omega, \tau) = \left| \int \tilde{\mathcal{E}}(\Omega - \omega) \tilde{\mathcal{E}}(\omega) \exp(i\omega\tau)\, d\omega \right|^2 \tag{32}$$

and

$$\begin{aligned} R(\Omega) = Q(\Omega) \frac{\Omega^3}{n_E(\Omega)} \left[\left(n_E^2(\Omega) - 1\right) \left(n_O^2(\Omega/2) - 1\right)^2 \right]^2 \\ \times \operatorname{sinc}^2 \left(\frac{\Delta k(\Omega/2, \Omega/2) L}{2} \right). \end{aligned} \tag{33}$$

In (31)–(33), we retained only the terms that are Ω-dependent.

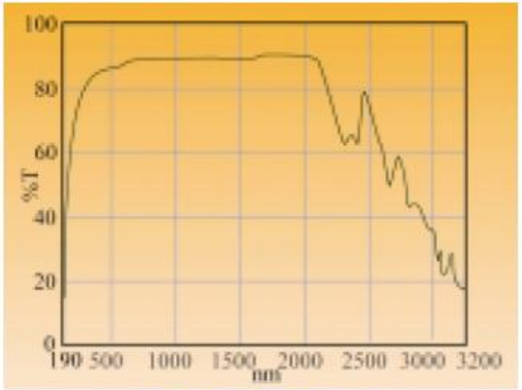
Second- and Third-Harmonic Generation (SHG/THG)

400nm (**SHG**, UV)

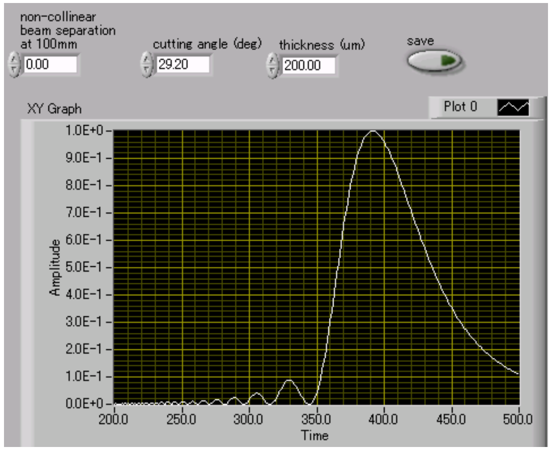
- $v_{g,SH} \sim v_{g,fund}$
- large $\chi^{(2)}$
- no absorption for fund/SH
- no two-photon absorption for SH

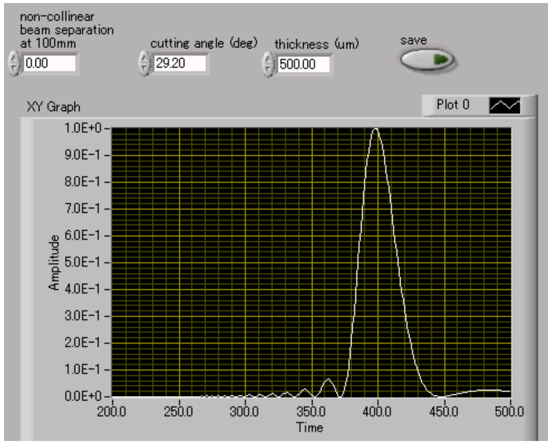
typical choice "BBO"
- 0.5mm for 80-100fs
- 0.2mm for 30fs

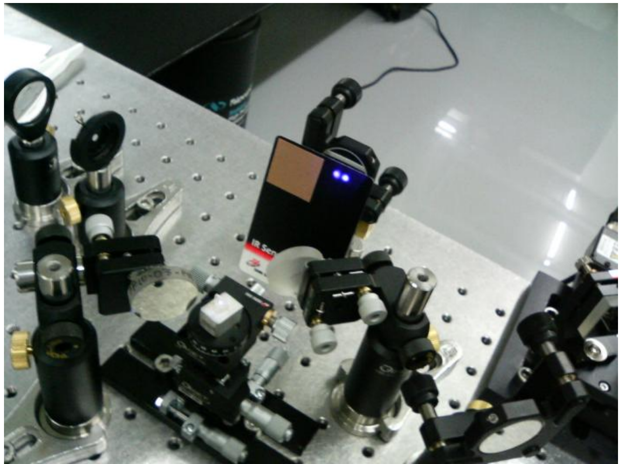
40-50% conversion eff.

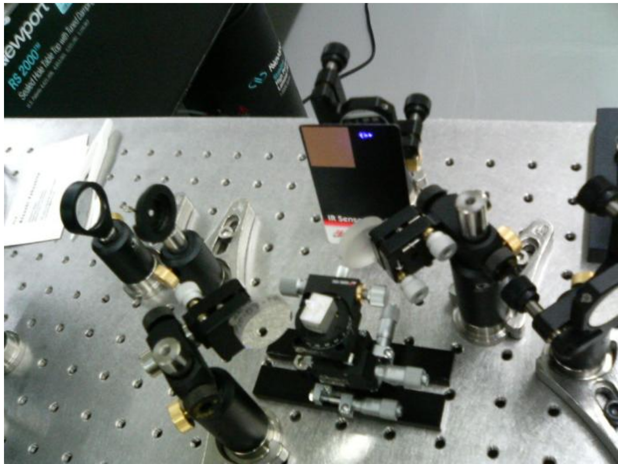


BBO 波長透過特性(厚み＝7mm)

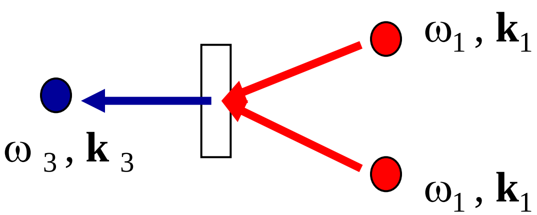




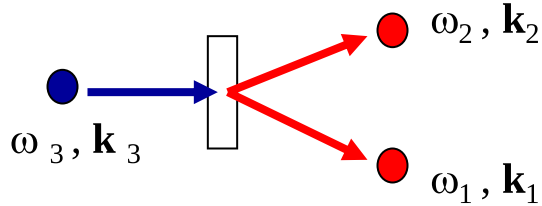




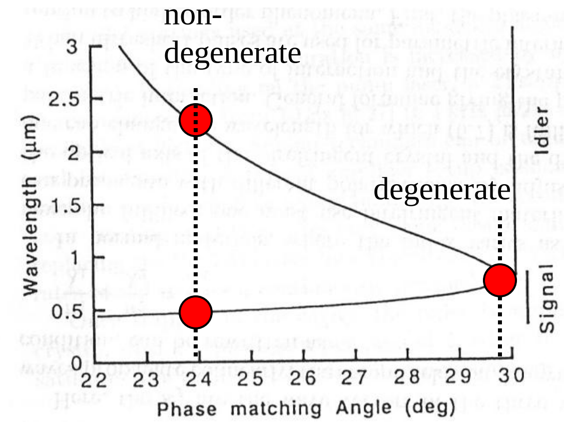
Optical Parametric Generator/Amplifier (OPG/OPA)

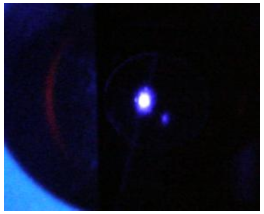


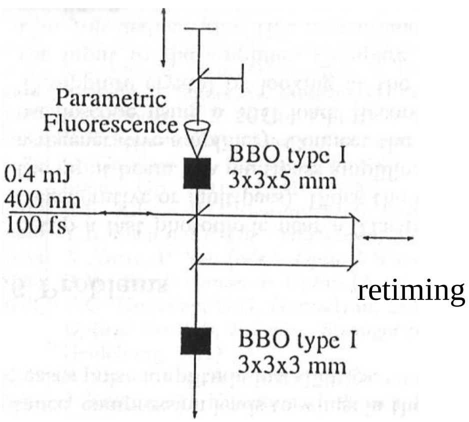
SHG (*ex.* IR to vis)



OPG (*ex.* UV to vis)







parametric amp. gain ~ 10^6/pass

(a photon of 10^{-19}J to 1μJ after 2 pass)

thermal agitation can cause OPG

phase match condition…limit/tune bandwidth

typical OPG : type-I 5mm-BBO, pumped by 50GW/cm^2

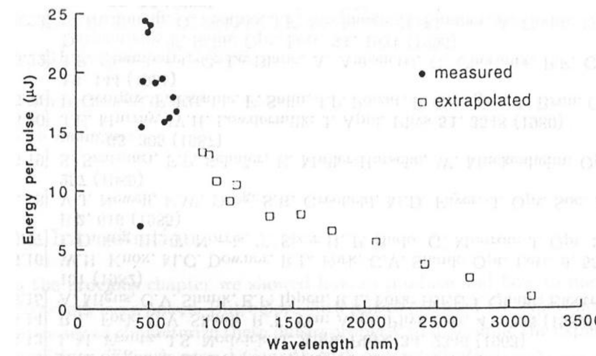
λ_{OPG}=450-2500nm, output ~ 3 μJ

~50μJ (1kHz), ~500μJ (10Hz) in use of 2nd BBO

typical tuning curve of OPG

(two-stage BBO, 1kHz pump by SH of Ti:S)

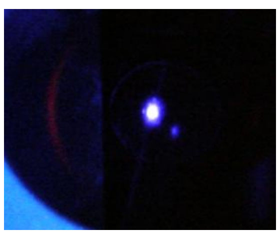
large GVD…retime at each stage, $\Delta\tau$>100fs



single-filament white-light continuum (WLC) *as a source of OPG*

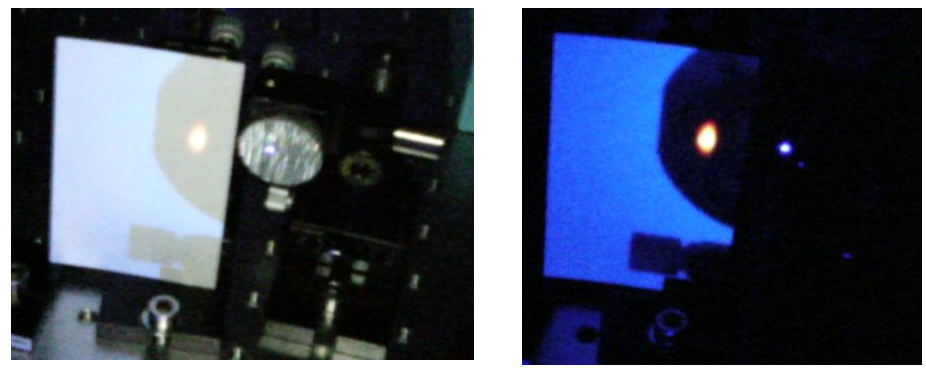
phase matched spectrum is amplified
high power coherent radiation
diffraction-limited WLC

} ***tunable*** ***high-power*** ***diffraction-limited***

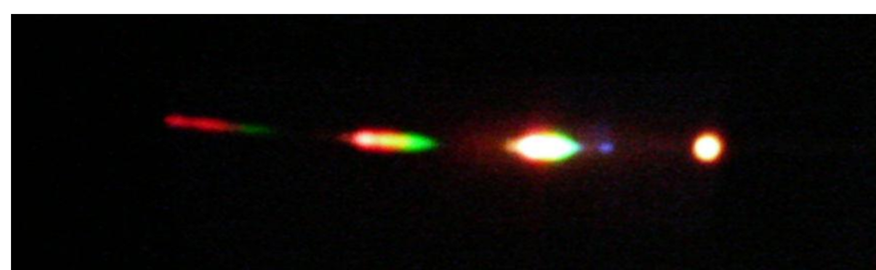


OPG

WLC



OPA (OPG with WLC)



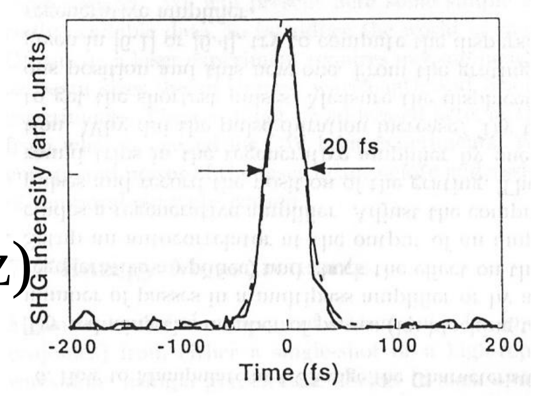
OPG pumped by 800nm

1-3.2μm (BBO), -4μm (KTP), -5μm ($KNbO_3$)

$v_{g,pump}$~$v_{g,signal}$…longer crystal

20fs, 1.3μm in type-I BBO OPG (~100μJ at 1kHz)

visible by mixing with 800nm,



DFG (difference-frequency generation) for **MIR**

1.5μm (signal) and 1.7μm (idler) of 1st OPG…DFG=**13μm**

$AgGaS_2$, $AgGaSe_2$, $ZnGeP_2$, etc…

large difference between v_g(1.6μm) and v_g(10μm)

cannot be short pulse

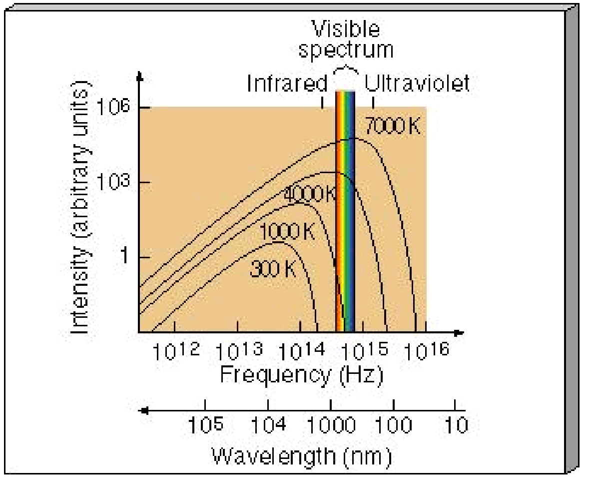
excite vibration/rotation modes of molecules

(***ex.*** microwave oven for H_2O)

spectral region ~ blackbody at 300K

it means…

fingerprint region (650-1350cm^{-1})



NonCollinear Optical Parametric Amplifier (NOPA)

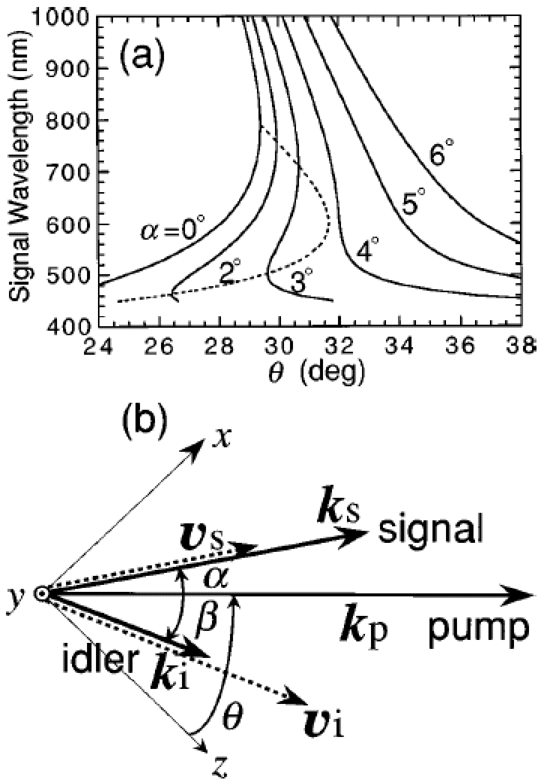


FIG. 1. (a) Theoretical phase-matching curves of type-I BBO OPA pumped at 395 nm with different noncollinear angles α. The dashed line indicates the GV matching points between the signal and idler pulses. (b) Geometry of the noncollinear phase matching. The wave vectors of the pump ($\mathbf{k}_p$), signal ($\mathbf{k}_s$), and idler ($\mathbf{k}_i$) are shown in the BBO crystal. The group velocities of the signal ($\mathbf{v}_s$) and idler ($\mathbf{v}_i$) are also shown by dashed lines. α and β are internal angles.

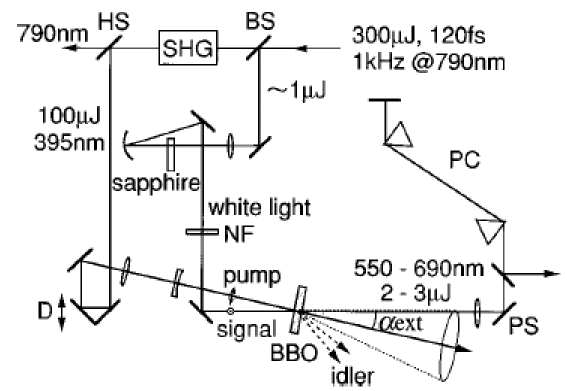


FIG. 2. Schematic of the noncollinearly phase-matched OPA. SHG:second harmonic generator, BS:beam sampler, HS:fundamental and second harmonic separator, NF:notch filter centered at 800 nm, D:variable optical delay-line, PS:periscope for rotating the polarization of the signal, PC:prism compressor. The conelike parametric fluorescence with the minimized dispersion (see text) is illustrated with the external cone angle α_{ext}.

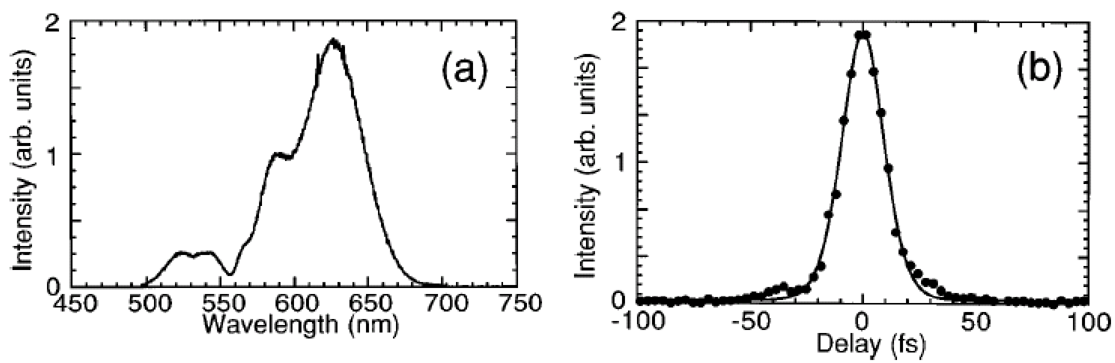


FIG. 3. (a) Spectrum of the signal centered at 625 nm. The FWHM is 66 nm corresponding to the bandwidth of ~1700 cm^{-1}. (b) Intensity autocorrelation trace (dots) after pulse compression. The sech^2 fit (solid line) with a pulse width of 14 fs (FWHM).

A. Shirakawa, T. Kobayashi, Noncollinearly phase-matched femtosecond optical parametric amplification with a 2000 cm^{-1} bandwidth, *App. Phy. Lett.* 72, 147 (1998)

example of NOPA (ALRC @ NCTU)

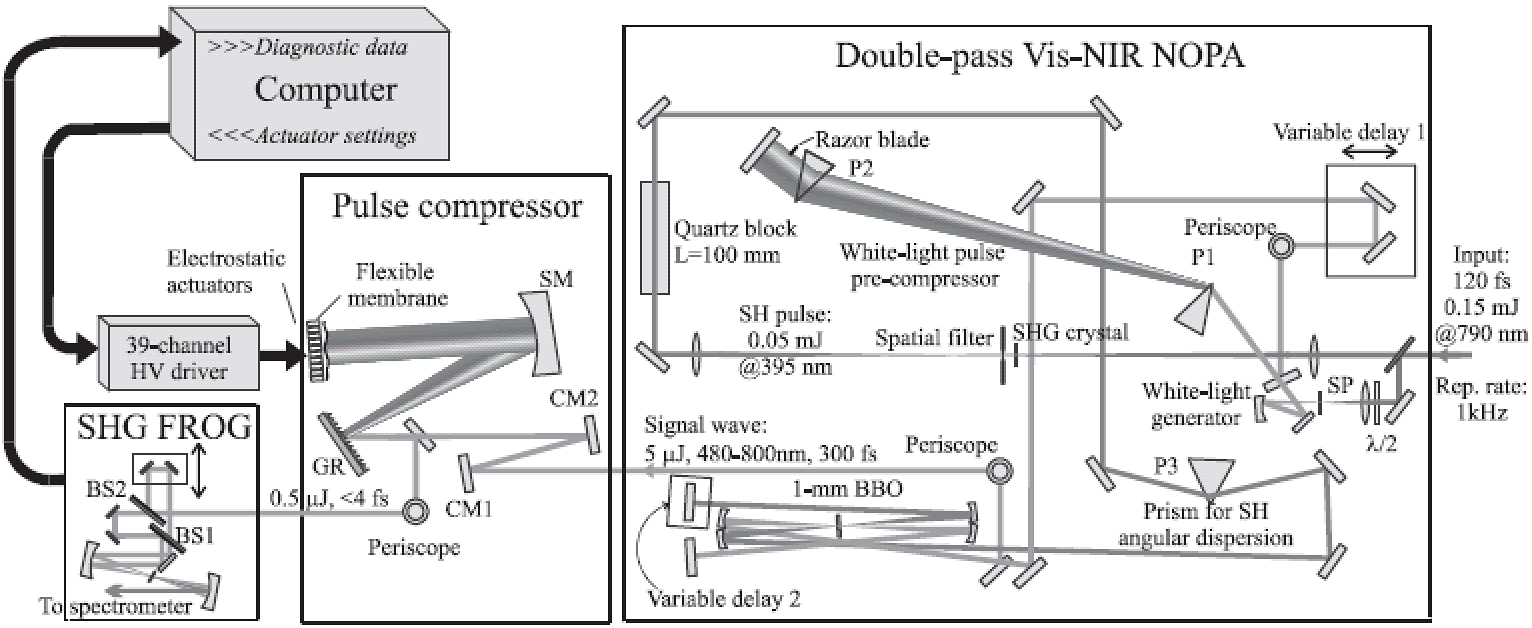
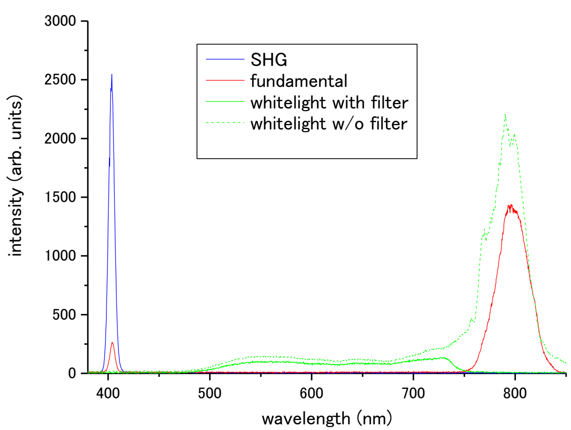
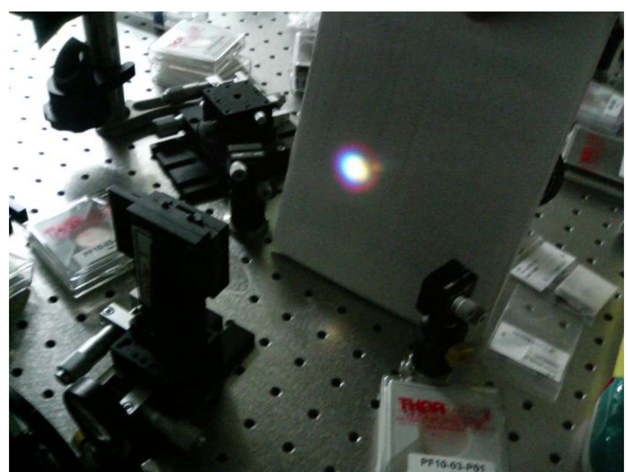
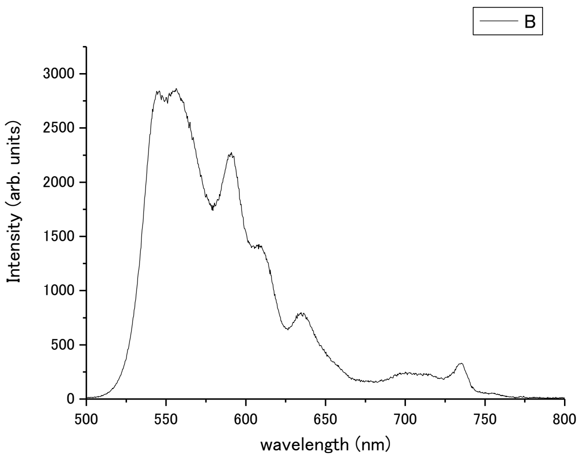


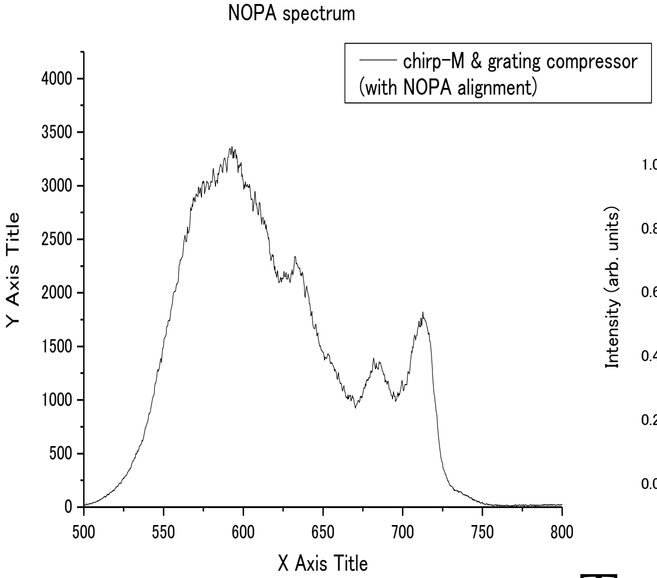
FIGURE 1 Schematic of experimental setup. λ/2: 800-nm wave-plate; SP: 2-mm sapphire plate; P1, 2: 45° quartz prisms; P3: 69° quartz prism, the distance from P3 to the NOPA crystal is 80 cm; CM1, 2: ultra-broadband chirped mirrors; GR: 300 lines/mm ruled diffraction grating (Jobin Yvon); SM: spherical mirror, $R = -400$ mm; BS1, 2: chromium-coated $d = 0.5$ mm quartz beam splitters. SHG crystal: 0.4-mm $\theta = 29°$ BBO (EKSMA); NOPA crystal: 1-mm $\theta = 31.5°$ BBO (Casix); SHG FROG crystal: $\theta = 29°$ BBO wedge plate $d = 5$–20 μm (EKSMA). Spherical mirrors around the NOPA crystal are $R = -200$ mm; *thick arrows* on the *left* indicate the data flow from the pulse diagnostics setup (SHG FROG) and the feedback to the flexible mirro

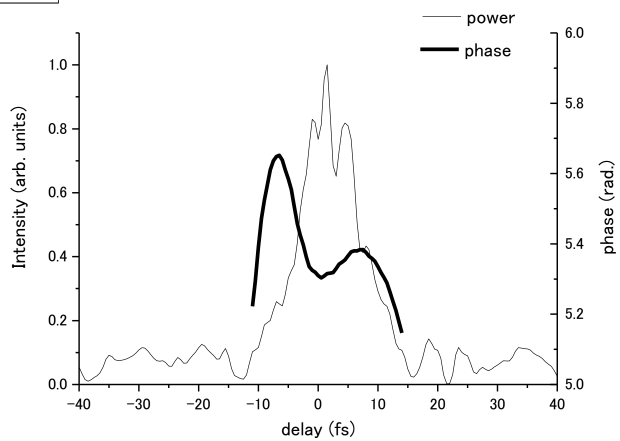




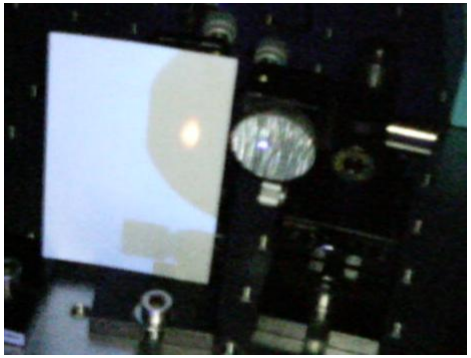
example of NOPA spectrum (ALRC @ NCTU)

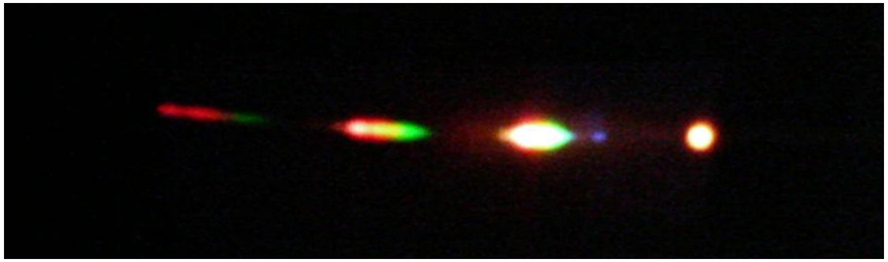




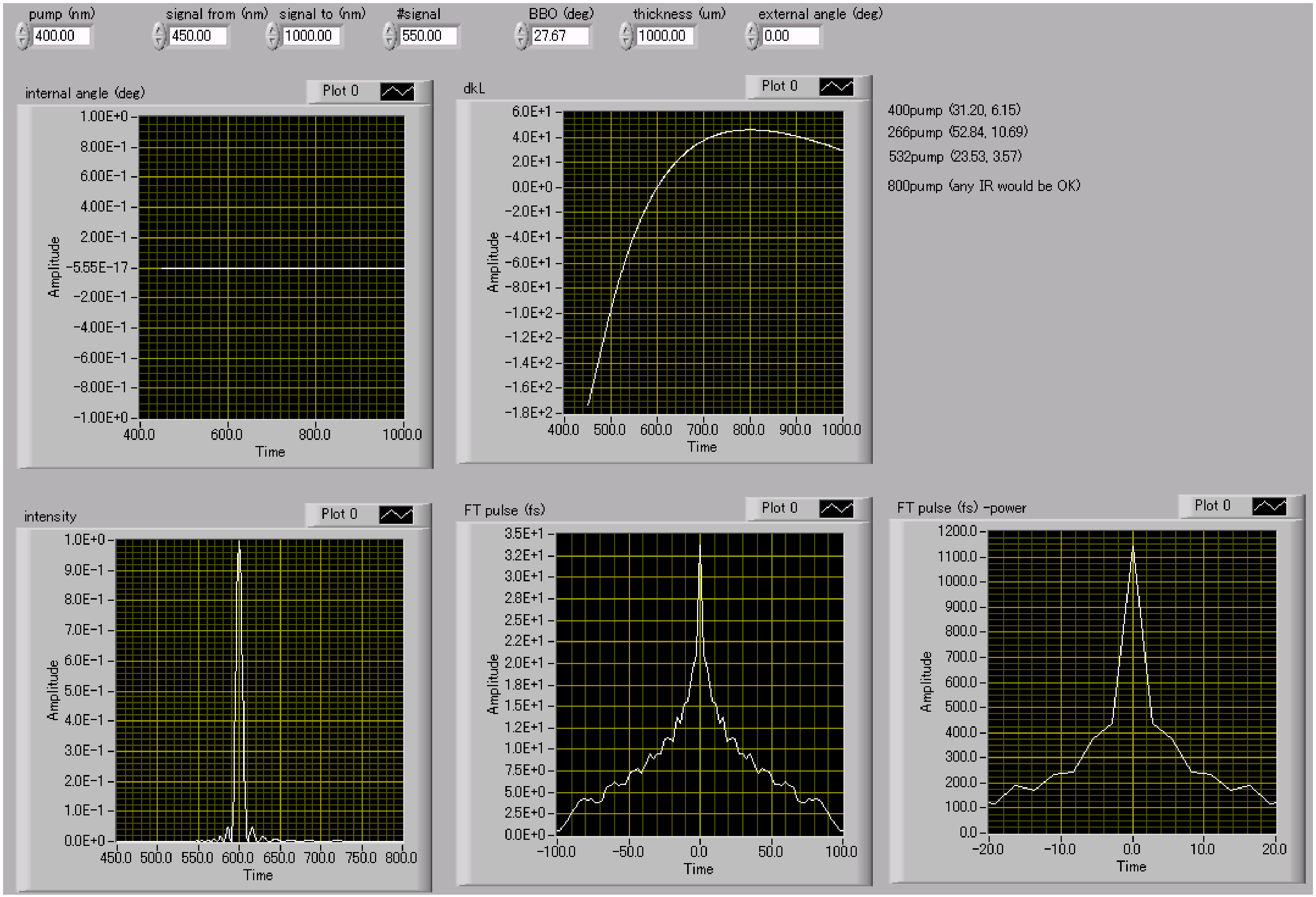


Temporal FWHM <10fs

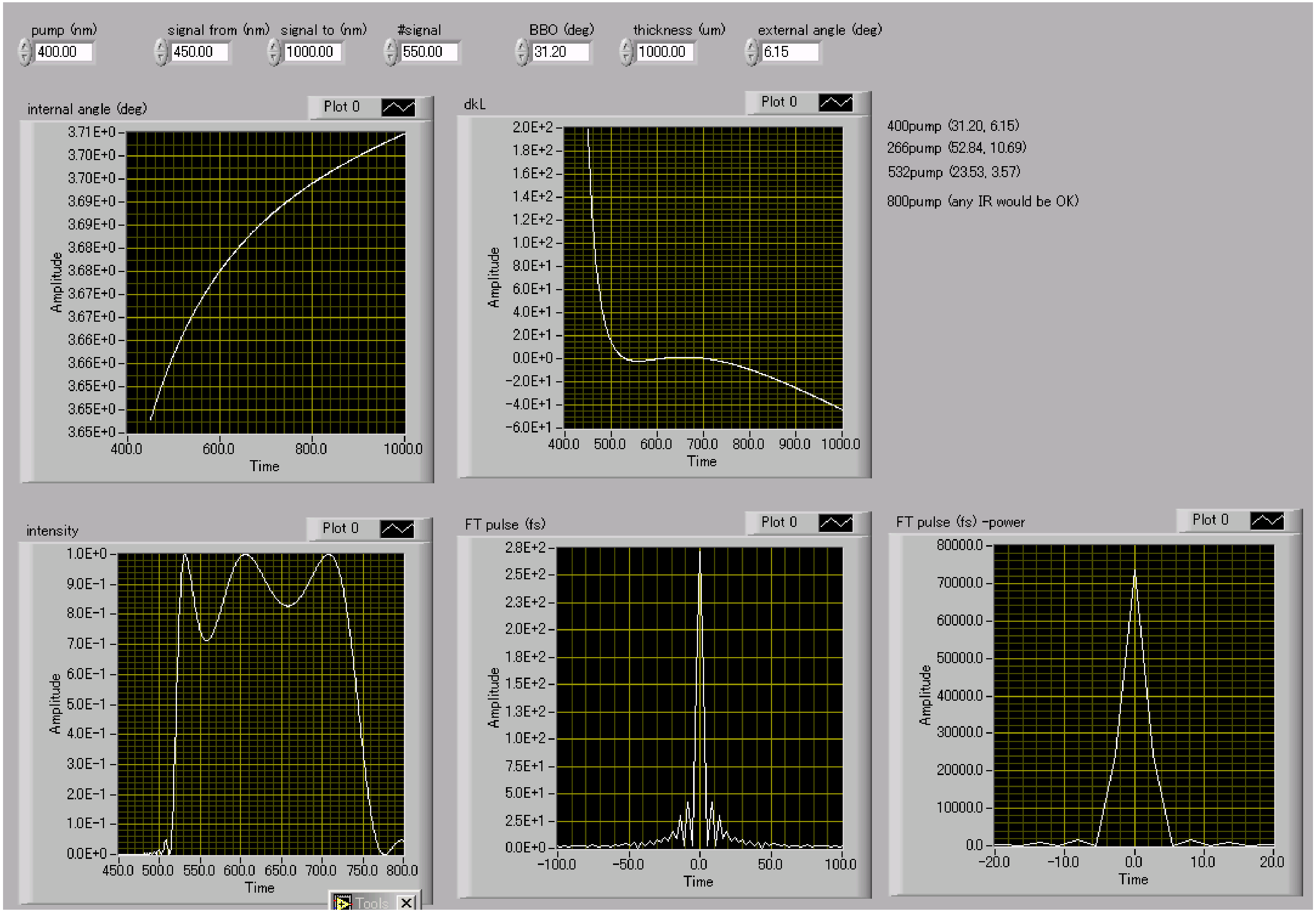




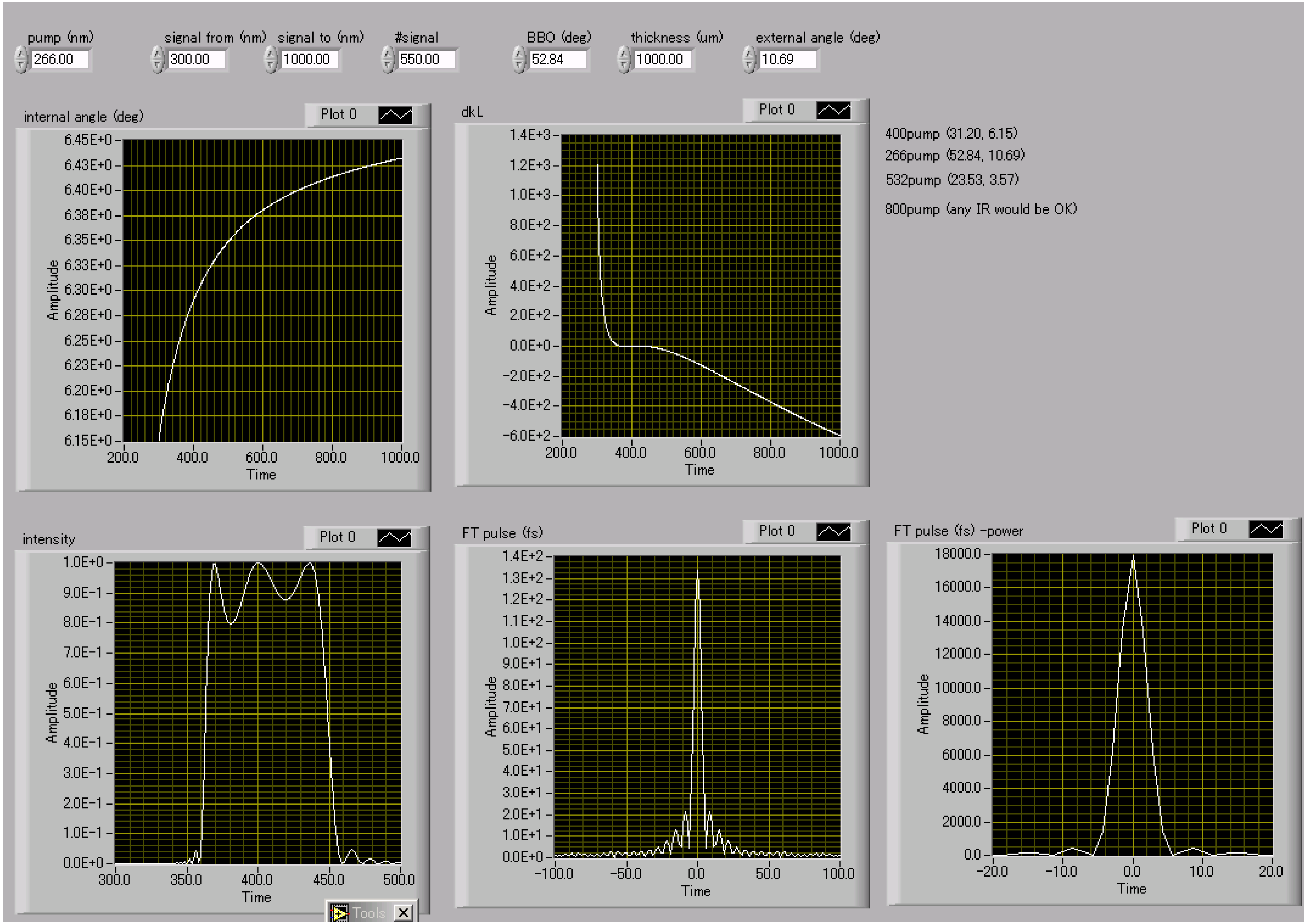
Simulation of OPA (pumped by SH-400nm)



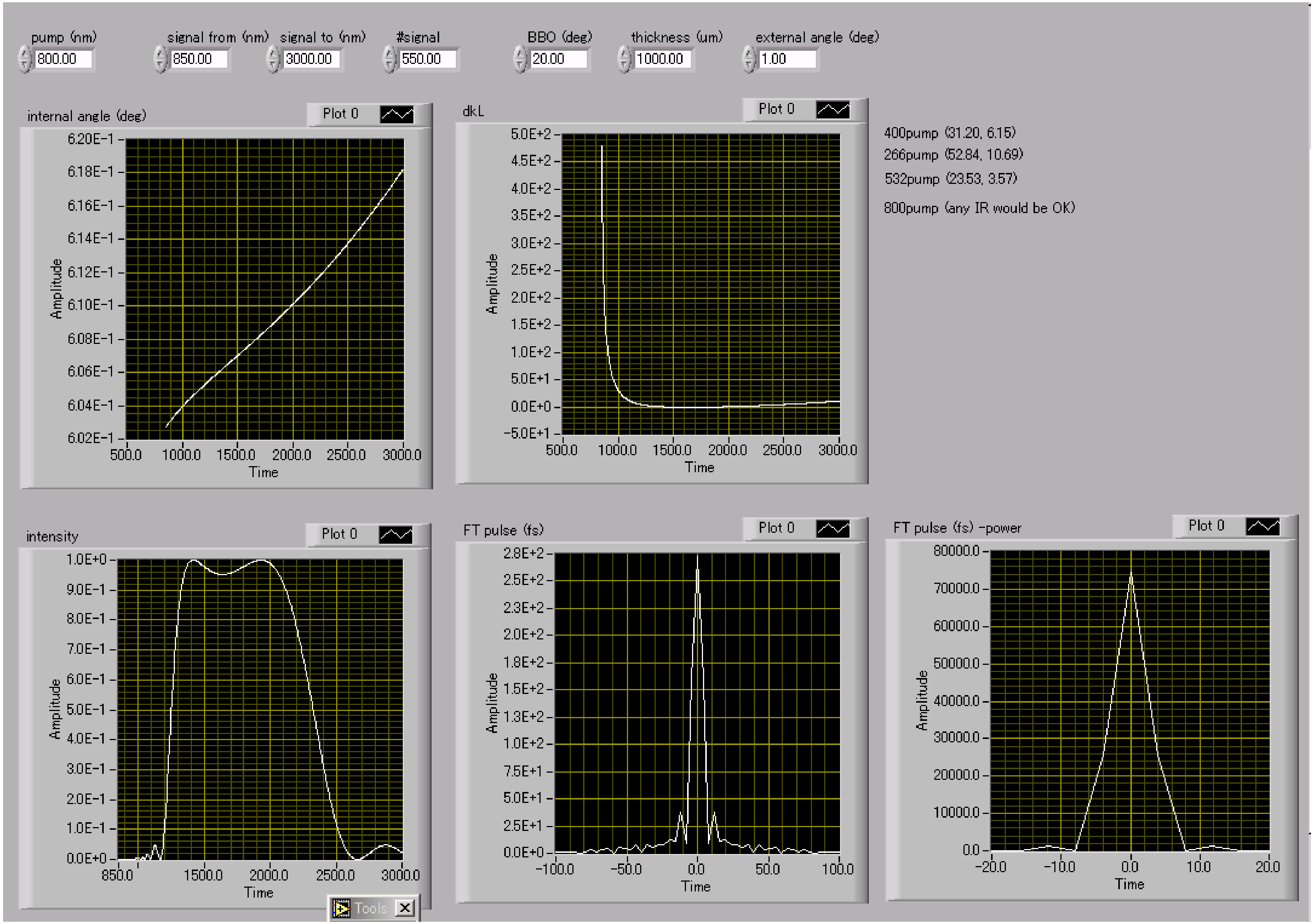
Simulation of NOPA (pumped by SH-400nm)
-sub 10fs in visible spectral range-



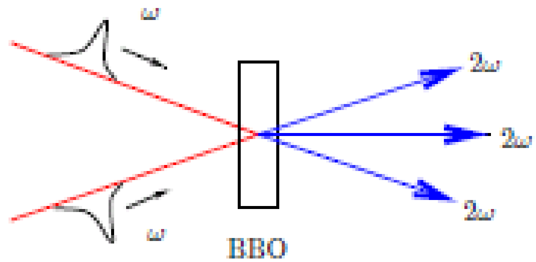
Simulation of NOPA (pumped by TH-266nm)
-sub 10fs in UV-VIS spectral range-



Simulation of NOPA (pumped by 800nm)
-sub 10fs in NIR spectral range-

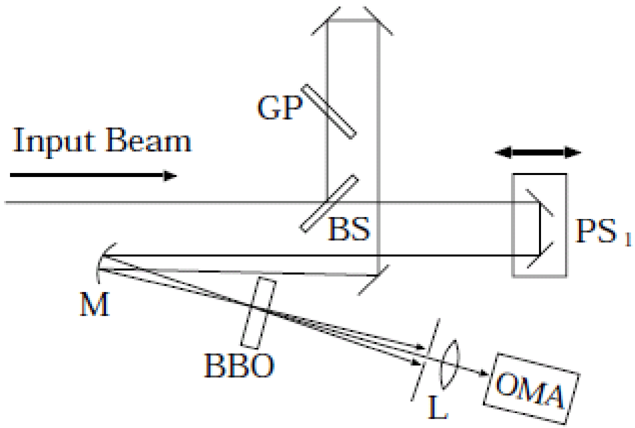


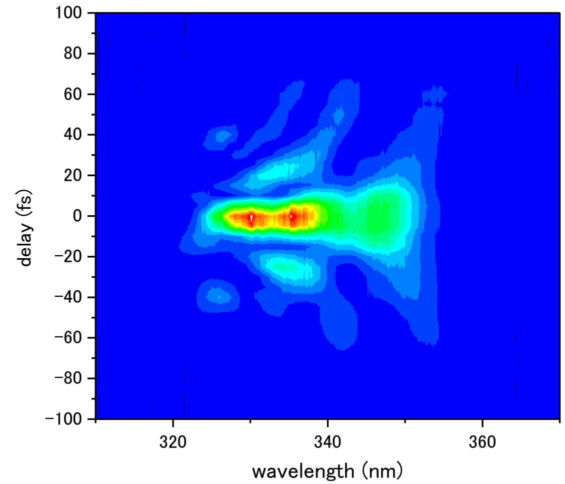
measure the Characteristics of Laser Pulses

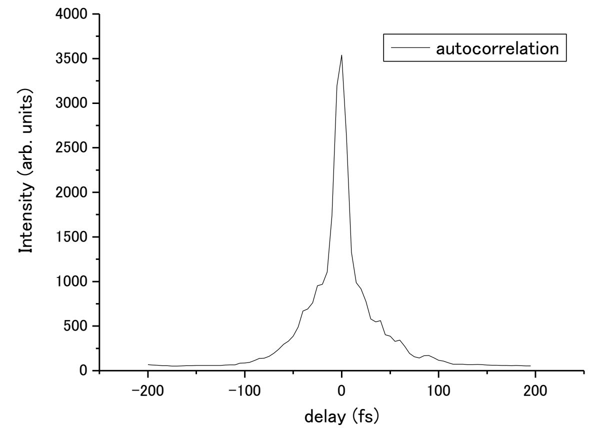


Frequency Resolved Optical Gating (FROG)

SHG-FROG







integration over λ

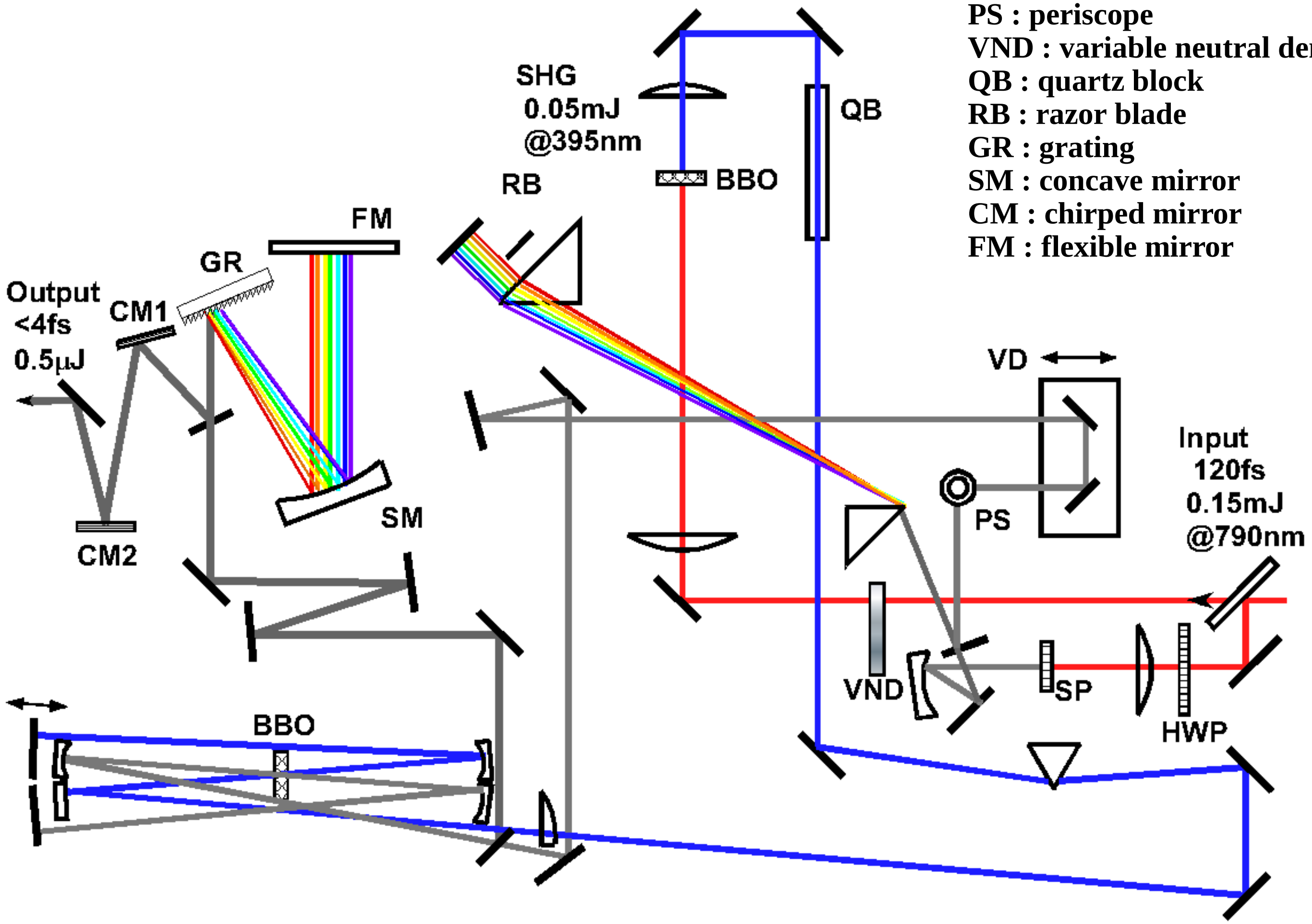
…autocorrelation

$$I_{\mathrm{FROG}}(\omega,\tau) = \left| \int_{-\infty}^{+\infty} E_{\mathrm{sig}}(t,\tau)\exp(\mathrm{i}\omega t)\,\mathrm{d}t \right|^2$$

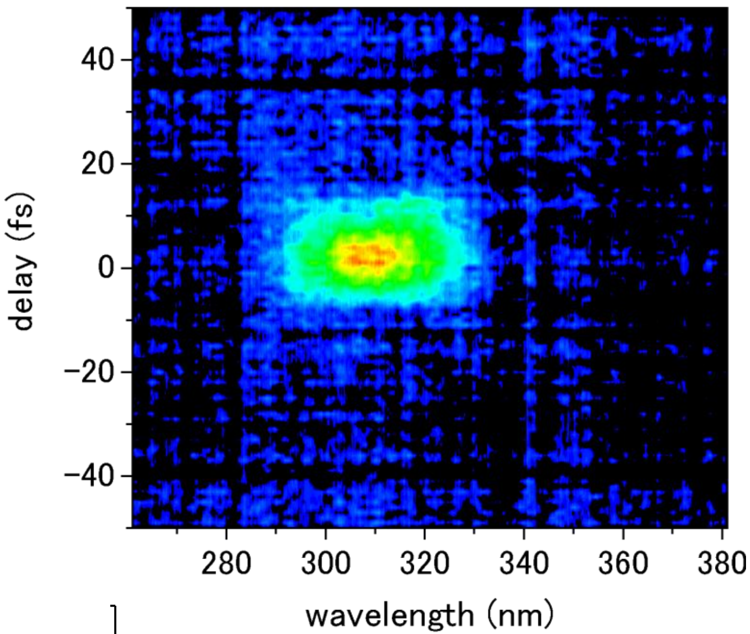
$$\begin{aligned}
M_\tau(\tau) &= \int_{-\infty}^{\infty} d\omega I_{\mathrm{FROG}}(\omega,\tau) \\
&= \int_{-\infty}^{\infty} d\omega \left| \int_{-\infty}^{\infty} dt E_{\mathrm{sig}}(t,\tau)\exp(i\omega t) \right|^2 \\
&= \int_{-\infty}^{\infty} d\omega \left| \int_{-\infty}^{\infty} dt E(t)E(t-\tau)\exp(i\omega t) \right|^2 \\
&= \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dt E(t)E(t-\tau)\exp(i\omega t) \int_{-\infty}^{\infty} dt' E^*(t')E^*(t'-\tau)\exp(-i\omega t') \\
&= \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' E(t)E(t-\tau)E^*(t')E^*(t'-\tau) \int_{-\infty}^{\infty} d\omega \exp(i\omega(t-t')) \\
&= \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' E(t)E(t-\tau)E^*(t')E^*(t'-\tau)\delta(t-t') \\
&= \int_{-\infty}^{\infty} dt E(t)E(t-\tau)E^*(t)E^*(t-\tau) \\
&= \int_{-\infty}^{\infty} dt I(t)I(t-\tau) \qquad (3.30)
\end{aligned}$$

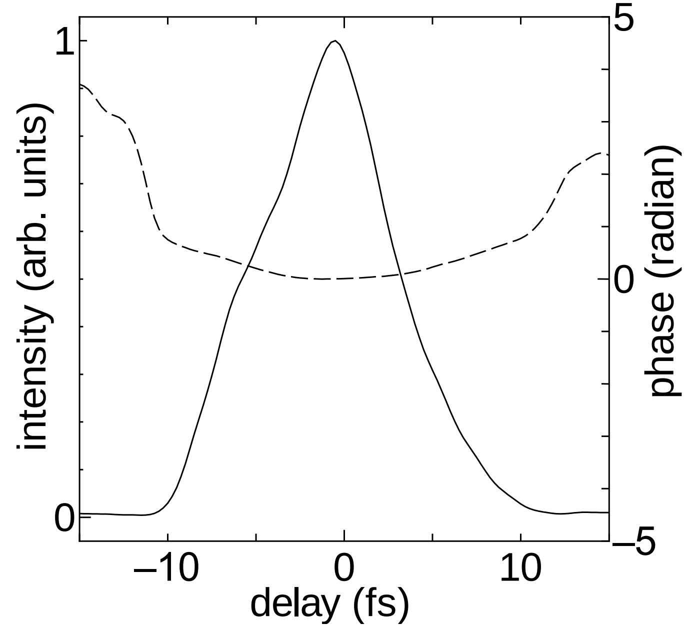
NOPA
(Noncolinear Optical Parametric Amplification)

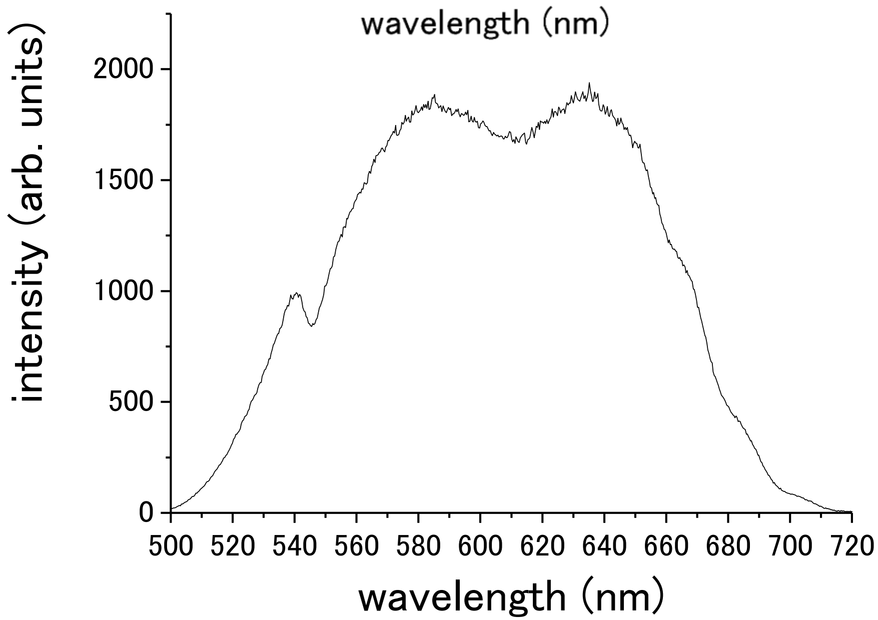
HWP : half wave plate
SP : sapphire plate
PS : periscope
VND : variable neutral density filter
QB : quartz block
RB : razor blade
GR : grating
SM : concave mirror
CM : chirped mirror
FM : flexible mirror



Character of the ultrashort visible laser pulse







FWHM:9.0fs

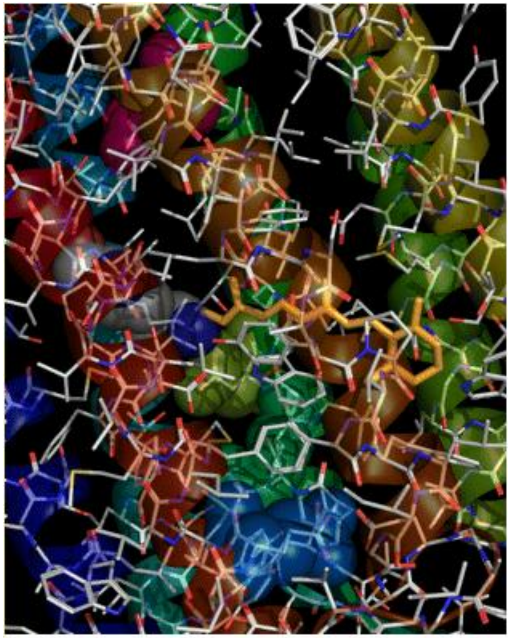
500-720nm (>6000cm^{-1})

1. Introduction
bacteriorhodopsin

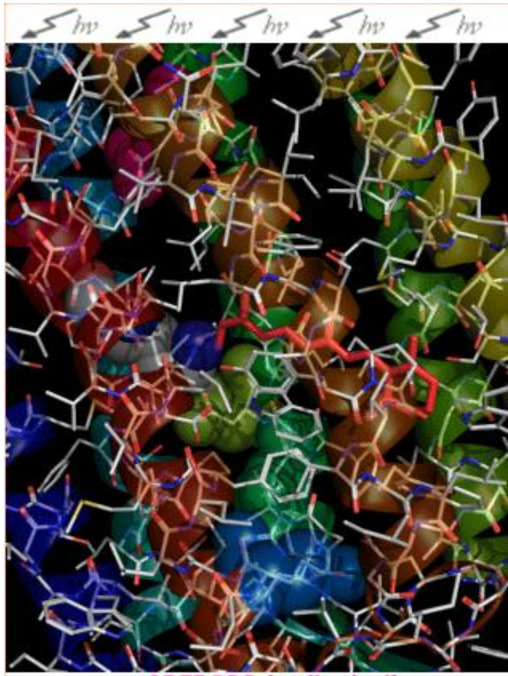
sample:bacteriorhodopsin(bR)

- Membrane protein
- Photoisomerization of retinal (all-trans→13-cis)

- proton pump
  transfer protons out of cells
  on photoisomerization

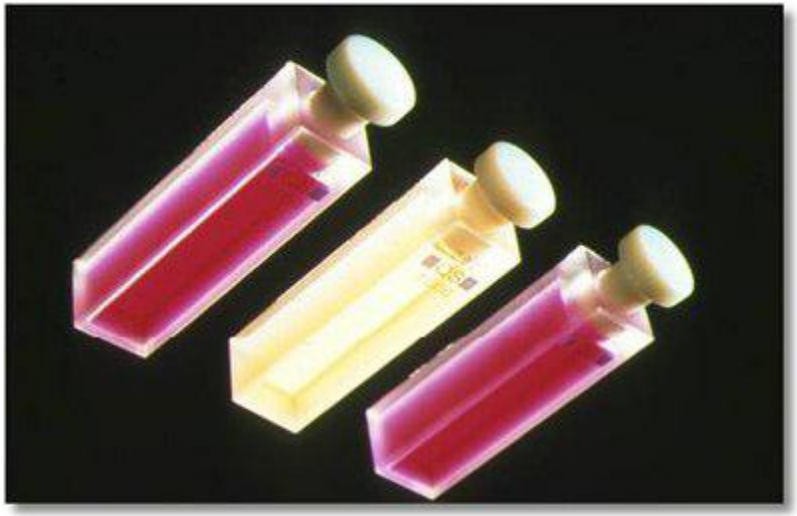


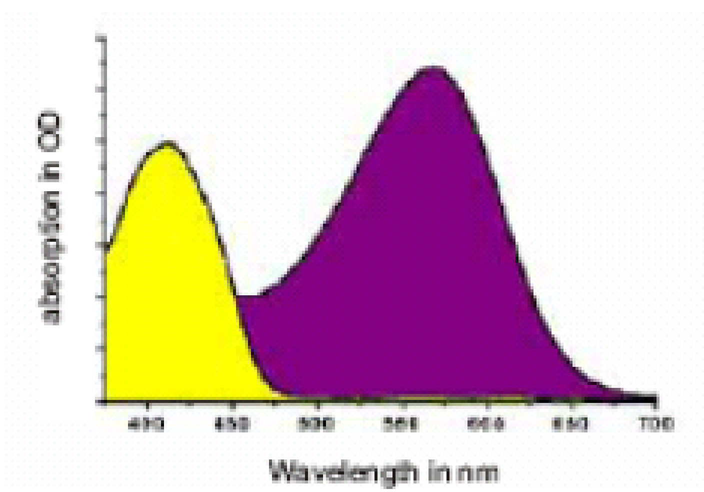
1C3W.PDB (ground state)

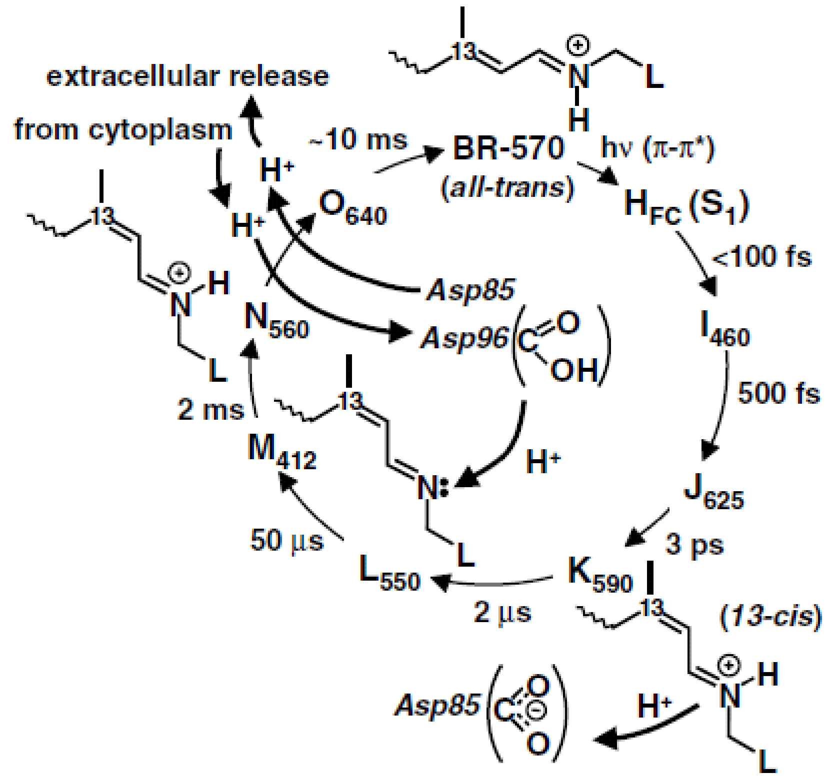


1DZE.PDB (activated)

1. Introduction (bacteriorhodopsin)





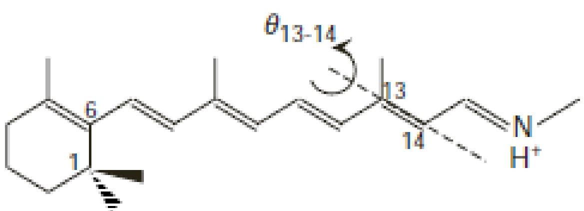


ultrafast photo-isomerization

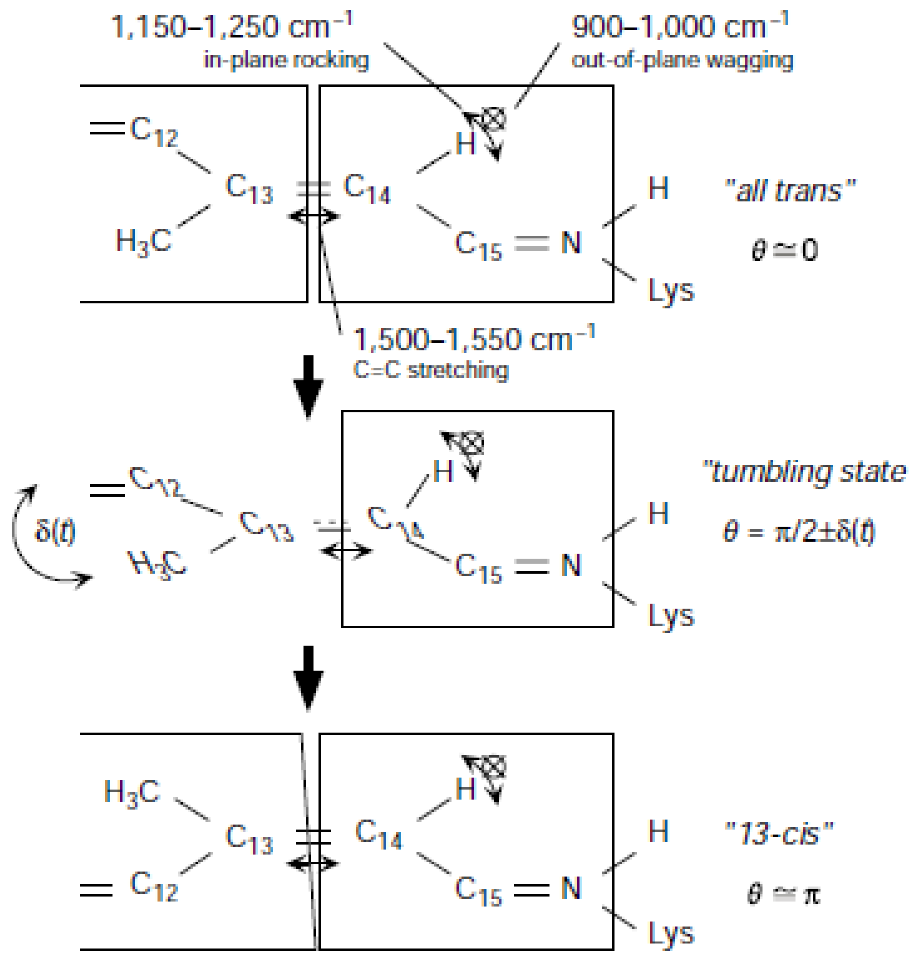
Photoisomerization of bacteriorhodopsin

$$bR_{568} \xrightarrow{h\nu} H \rightarrow I_{460} \rightarrow J_{625} \rightarrow K_{610} \rightarrow$$

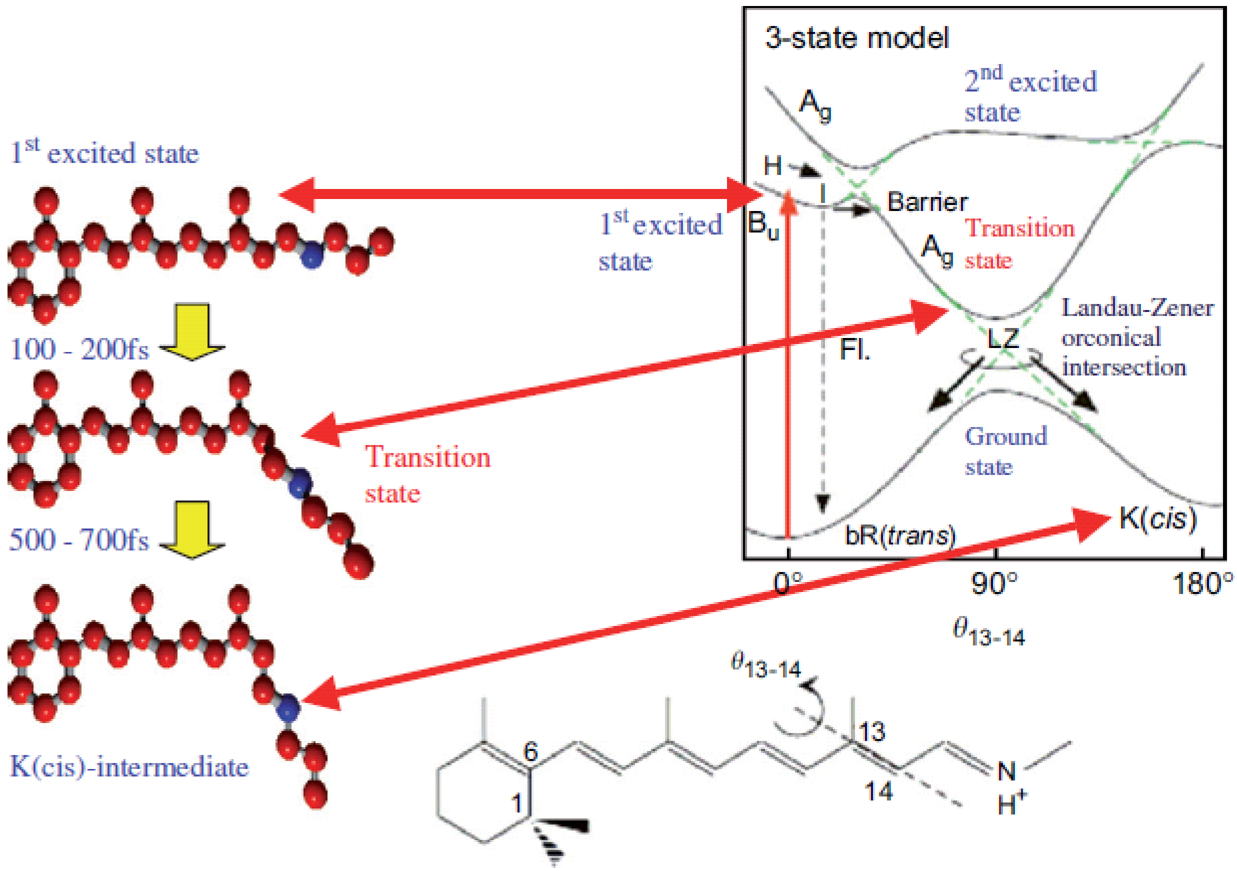
$$L_{543} \rightarrow M_{412} \rightarrow N_{560} \rightarrow O_{640} \rightarrow bR_{568}$$



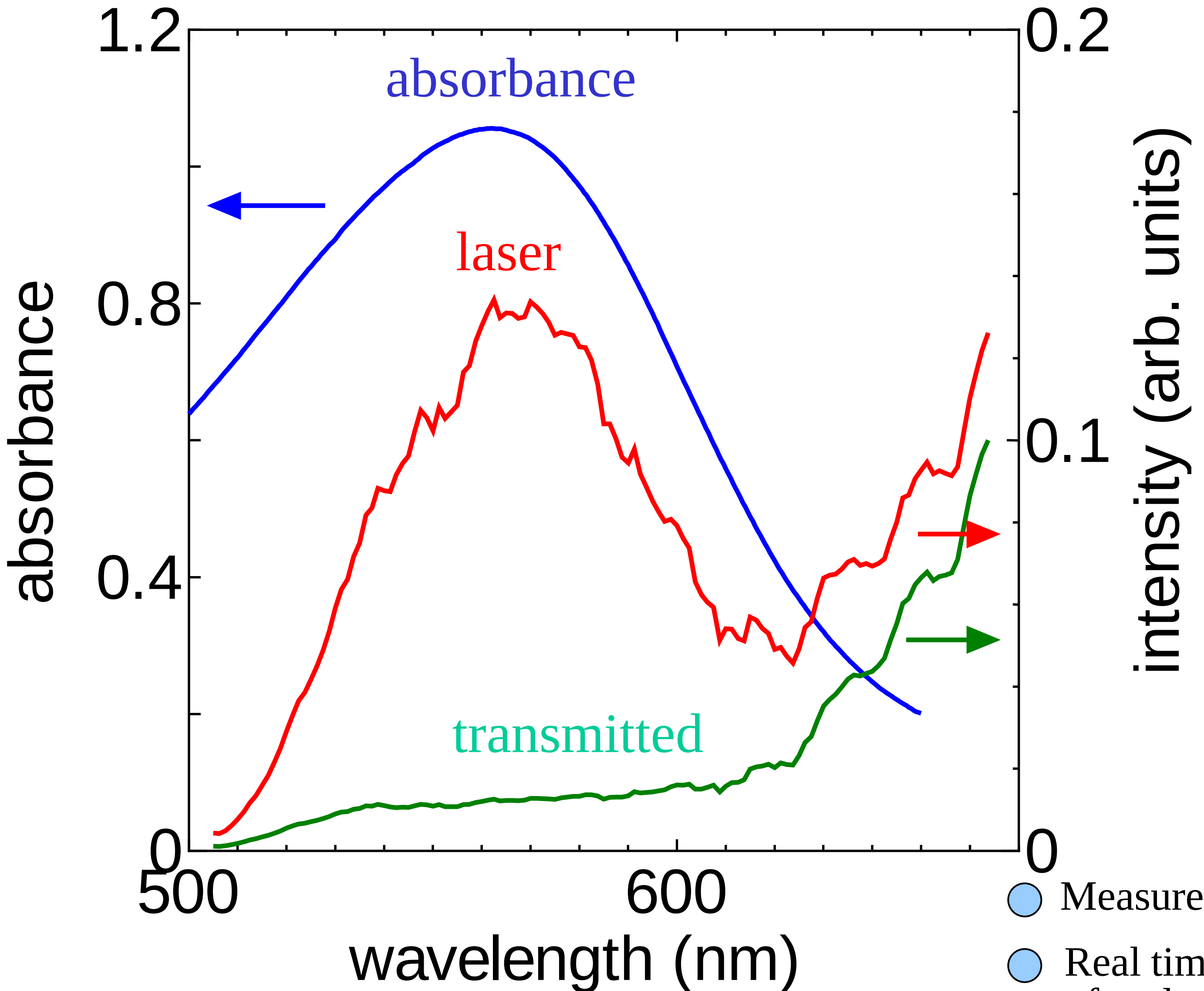
Photoisomerization of Retinal
(all-trans→13-cis)



initial processes in photo-isomerization of bR



Absorption spectrum of bR and laser spectrum



- Measurement in broadband
- Real time observation of molecular vibration (Ultrashort pulse)

2. Time-resolved absorption spectra (pump-probe)

"Pump-Probe" Methods

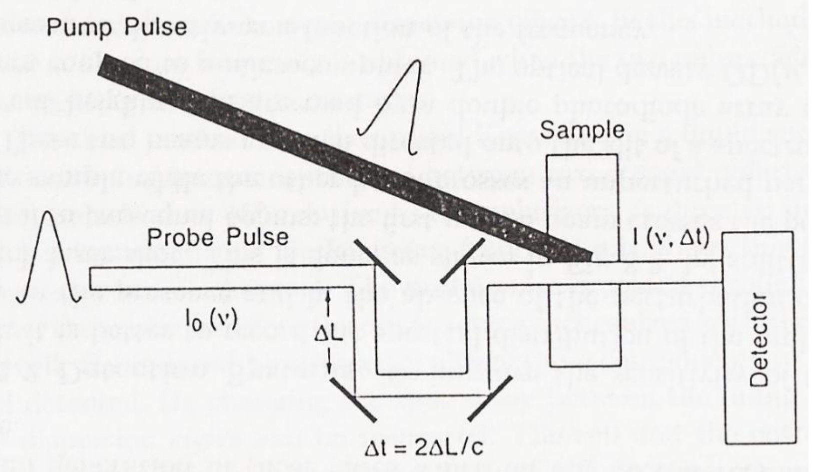


Fig. 8.1. Typical scheme of a "pump-probe" experiment

t=0 : pump perturbs the sample

t=Δt (tunable)
: probe crosses the perturbed sample

time-resolved absorption
difference before/after the cross on the perturbed sample

spectral change
new transition causes new absorption, transmission

absorbance change
increase/decrease of the optical density

spectral analysis : spectral change by electronic transition,…
signature of new photo-excited electronic states
(photochemical products, etc…)

temporal analysis : dynamics of transformation
(chemical reaction rates, etc…)

Beer-Lambert Law

$$I(\nu, \Delta t) = I_0(\nu) \times 10^{-\varepsilon_\nu N(\Delta t) l}$$

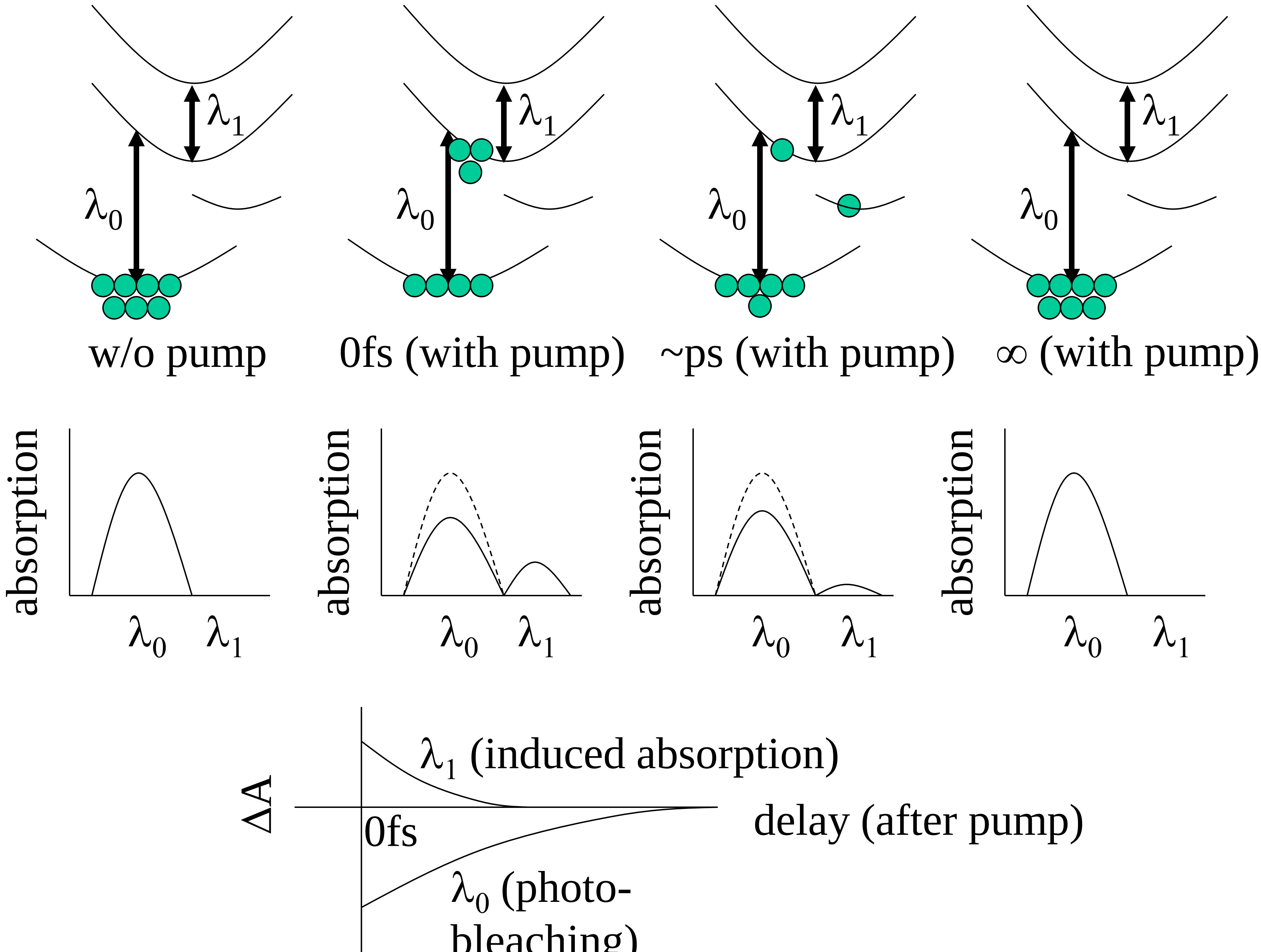
$I_0(\nu)$: probe intensity before the perturbed sample
$I(\nu, \Delta t)$: probe intensity after …
l : length of the sample
$N(\Delta t)$: population absorbing at Δt, ν
ε_ν : absorption coefficient of the sample at ν

optical density (OD) : quantify of interest

$$\text{OD } (\nu, \Delta t) = \log \frac{I_0(\nu)}{I(\nu, \Delta t)} = \varepsilon_\nu N(\Delta t) l$$

frequency-resolved OD (fix delay Δt, scan ν)
absorption spectrum of the excited state
time-resolved OD (fix ν, scan Δt)
dynamics of electronic population

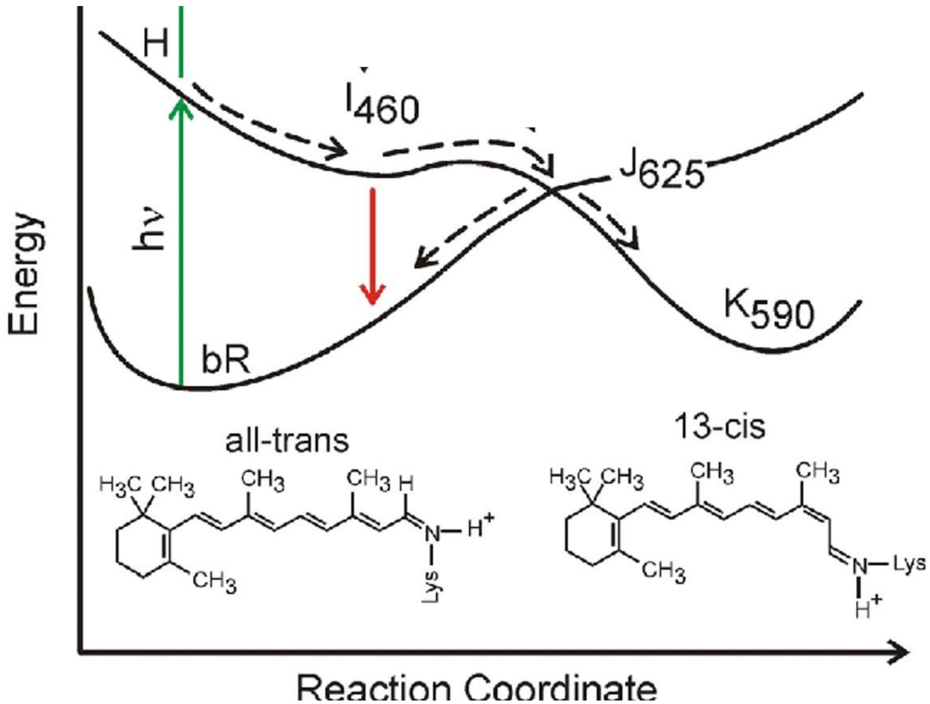
$$\ln \text{OD } (\Delta t) = \ln N(0) \varepsilon_\nu l - \Delta t / \tau$$


λ1
λ0
w/o pump
0fs (with pump)
~ps (with pump)
∞ (with pump)
absorption
λ0 λ1
ΔA
λ1 (induced absorption)
0fs
delay (after pump)
λ0 (photo-
bleaching)

3. Ultrafast dynamics
of electronic states

Scheme of the isomerization reaction of retinal in bR.

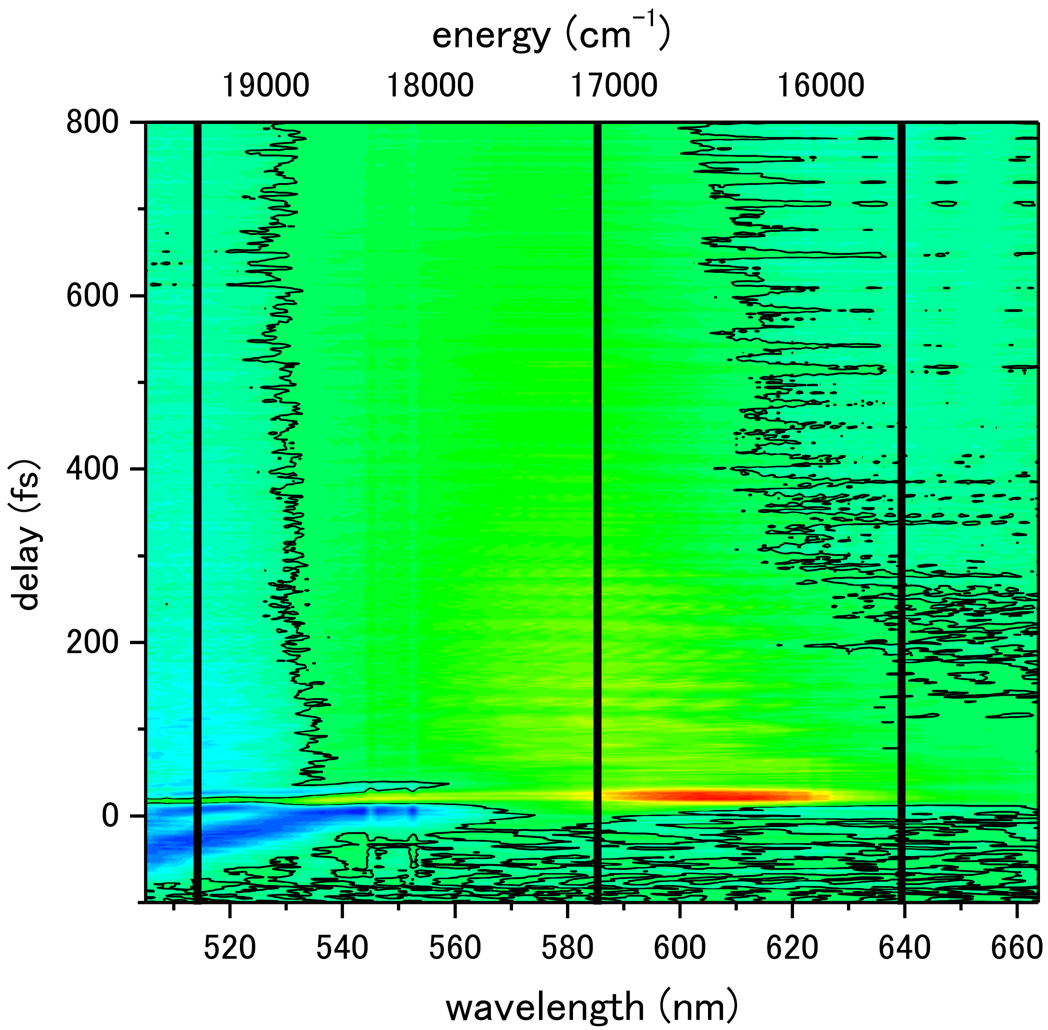
bR → H (200 fs) → I (500 fs) → J (3 ps) → K.



Florean A C et al. PNAS 2009;106:10896-10900

PNAS

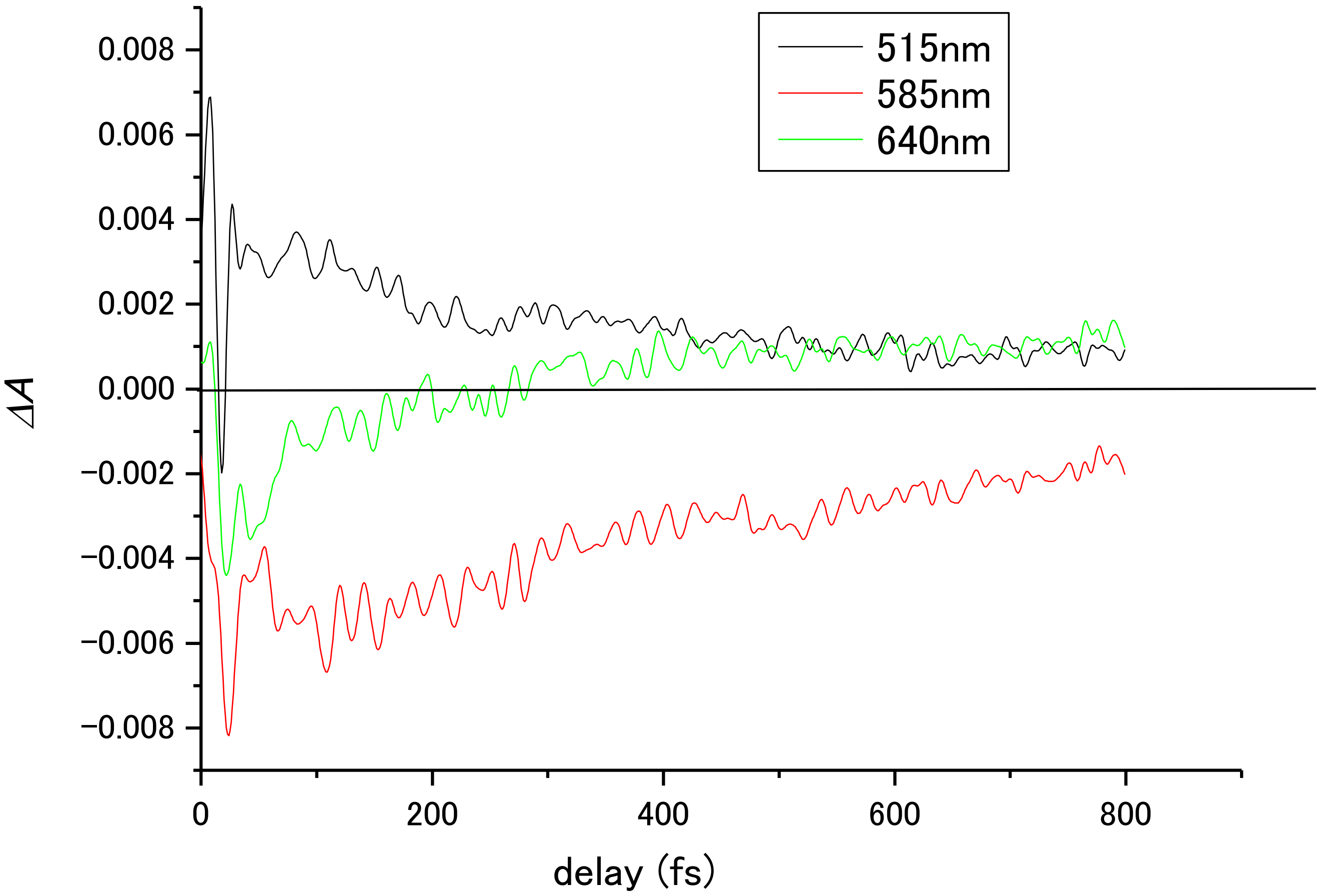
Transient absorption spectrum



Black curves (ΔA=0)

- **Induced absorption (left and right region)**
- **Bleaching (middle region)**

Transient absorption traces

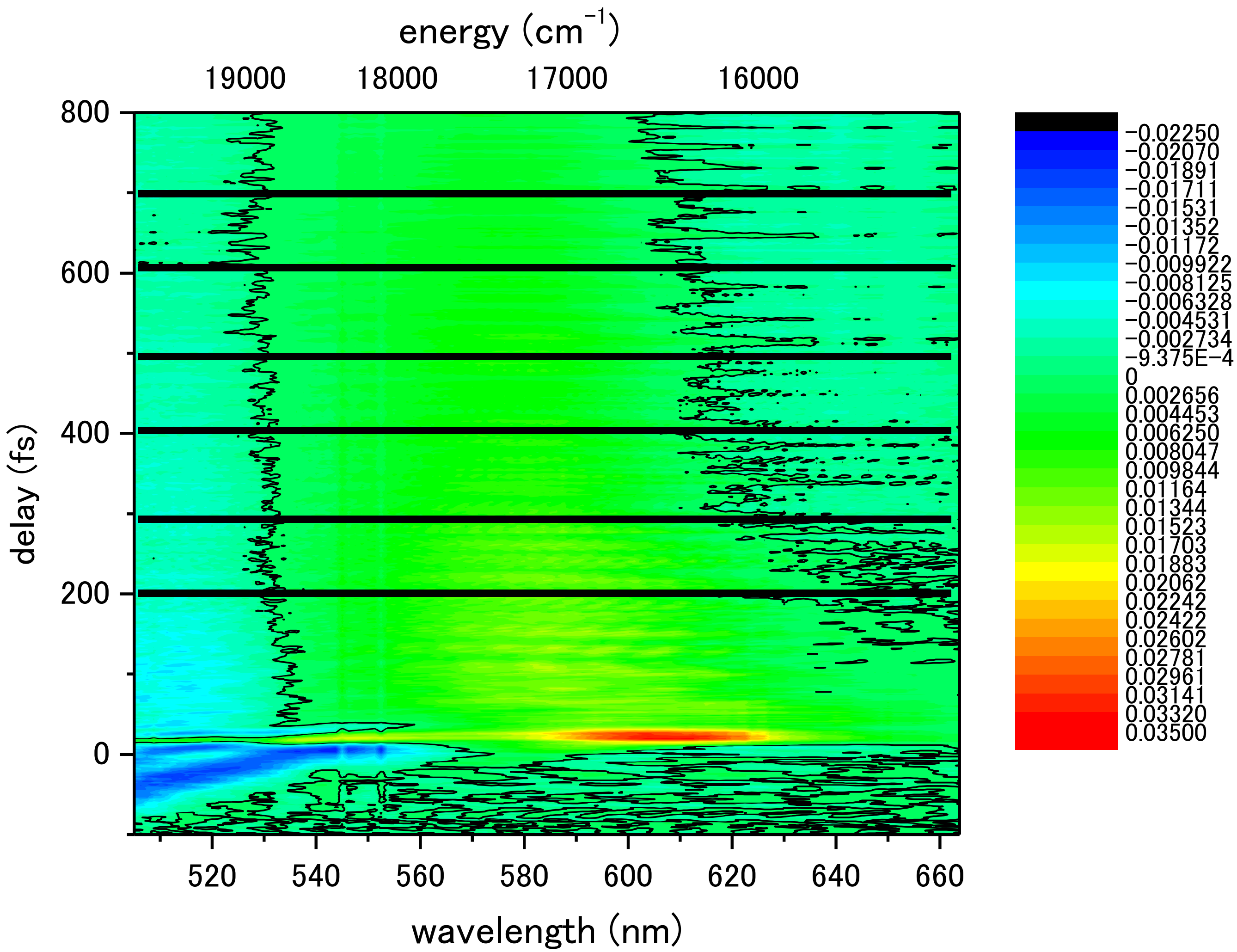


Transient absorption signal (induced absorption, bleaching)

Photo-excitation of G

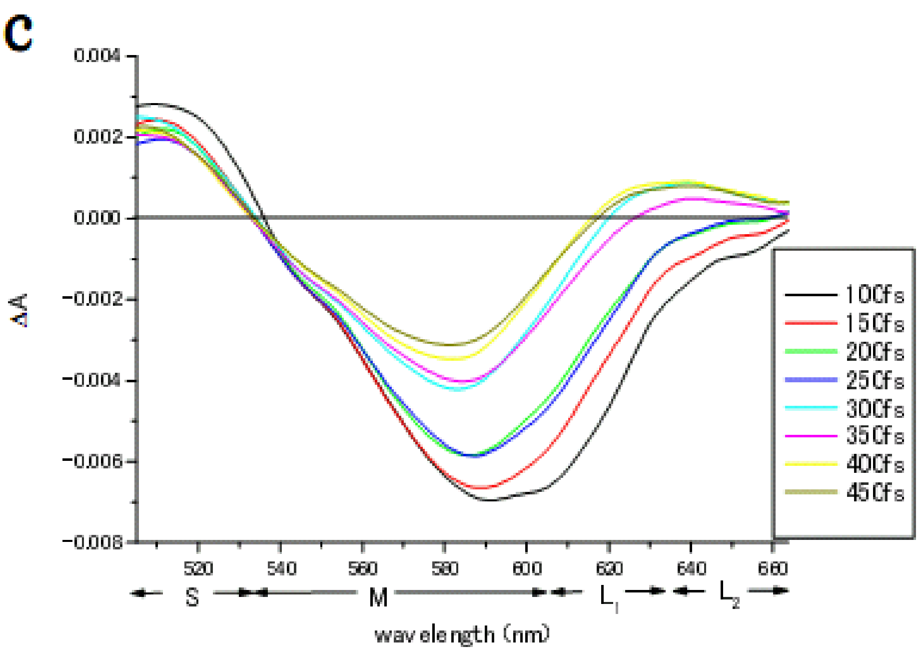
H-(~200fs)-I-(~500fs)-J-(~3ps)…

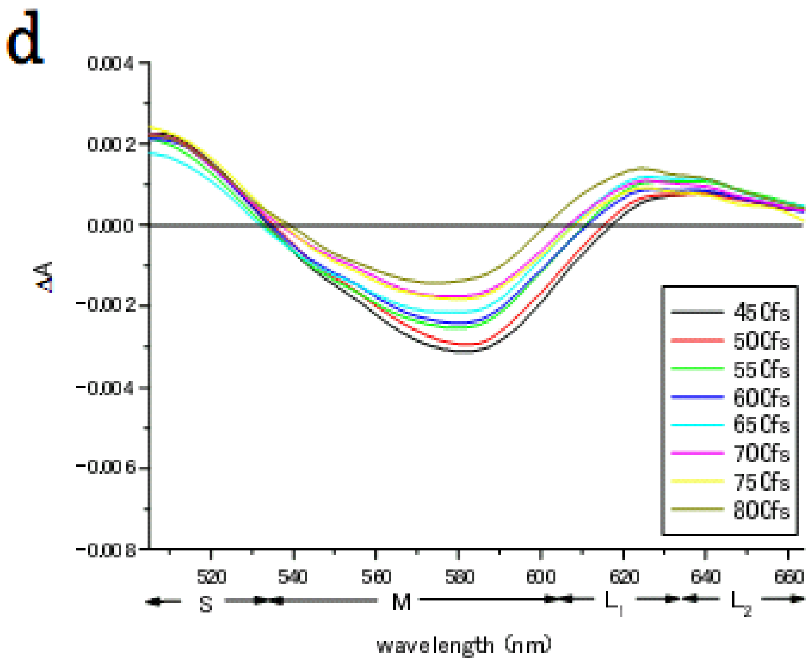
Transient absorption spectrum (dA−dT)



- **Induced absorption**
- **bleaching**

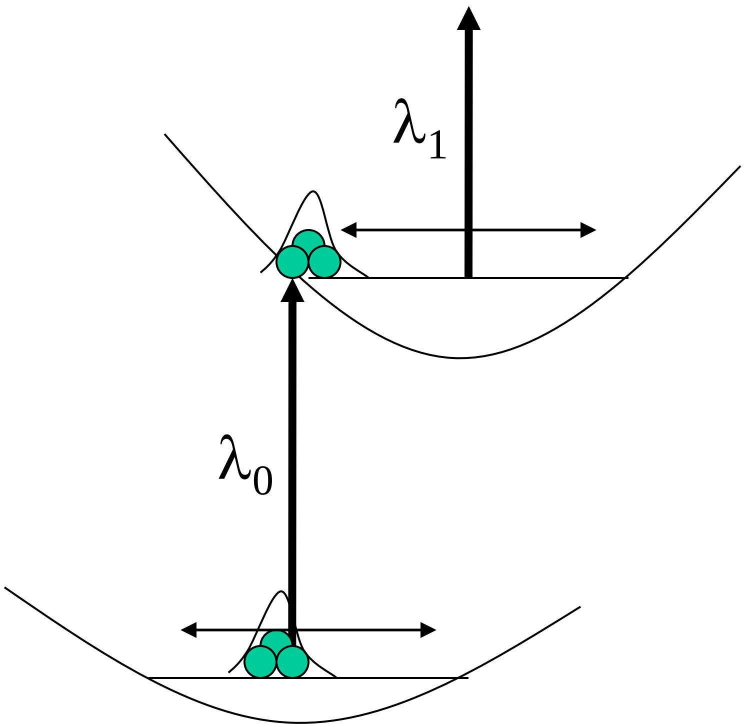
Transient absorption spectrum





- **Transient signal**
- **induced absorption**
- **bleaching**

4. Ultrafast dynamics of vibrational modes



Wave packet motion

caused by molecular vibration

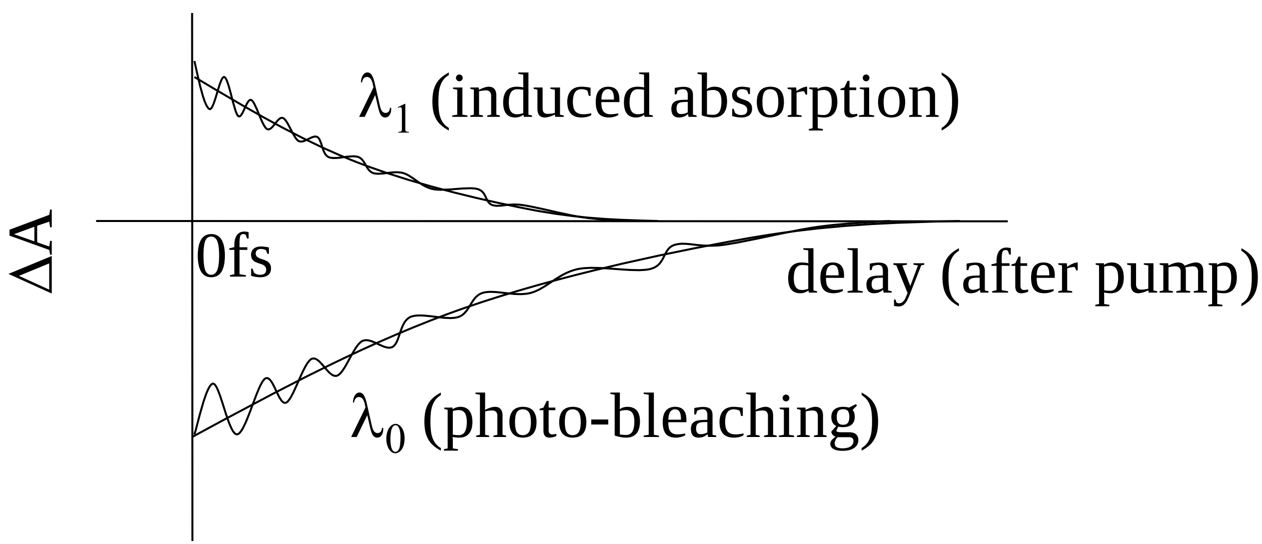
modulate ΔA signal

excited state (cosine-like)

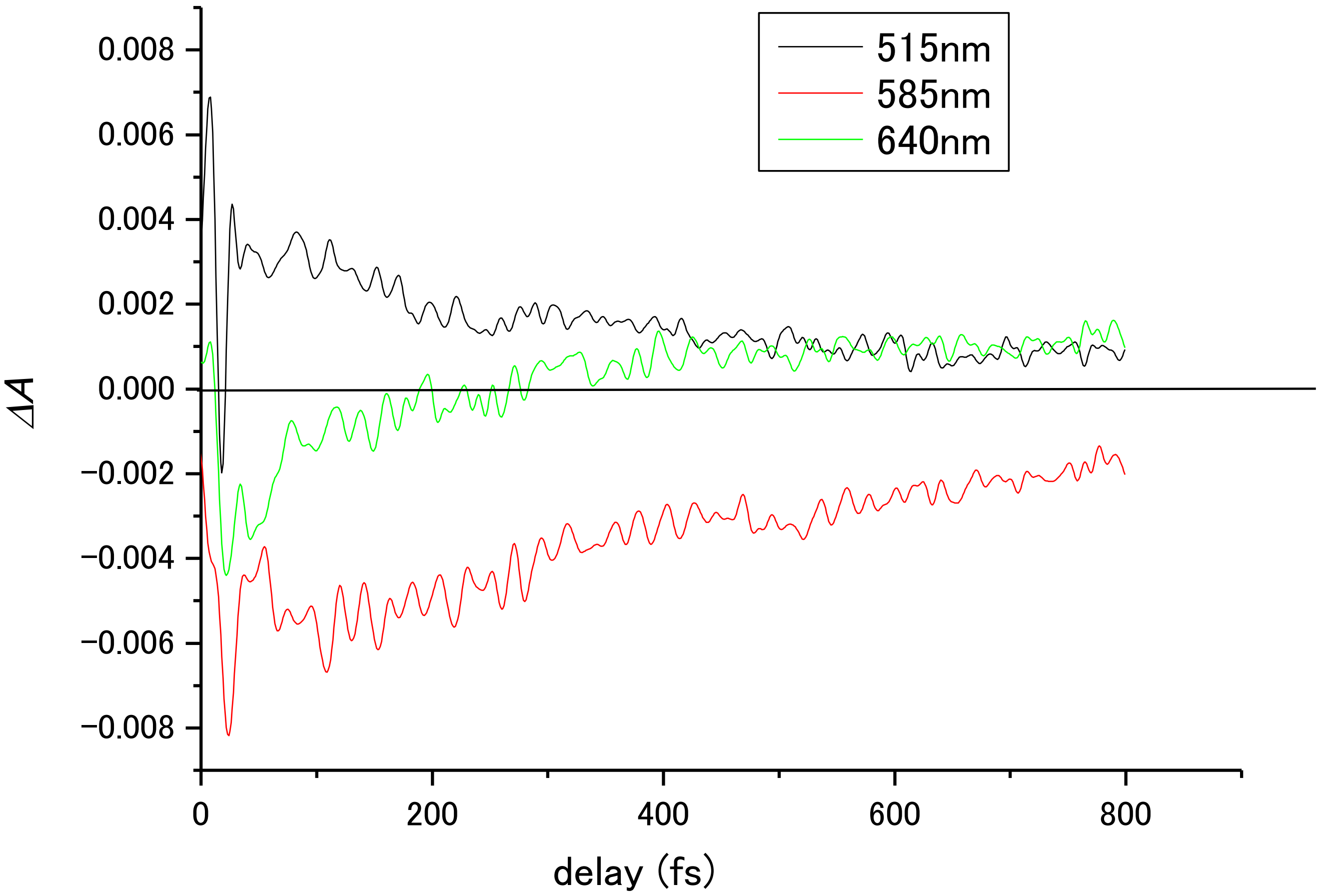
ground state (sine-like)

instantaneous vibration frequency

by time-gated FFT



Transient absorption traces



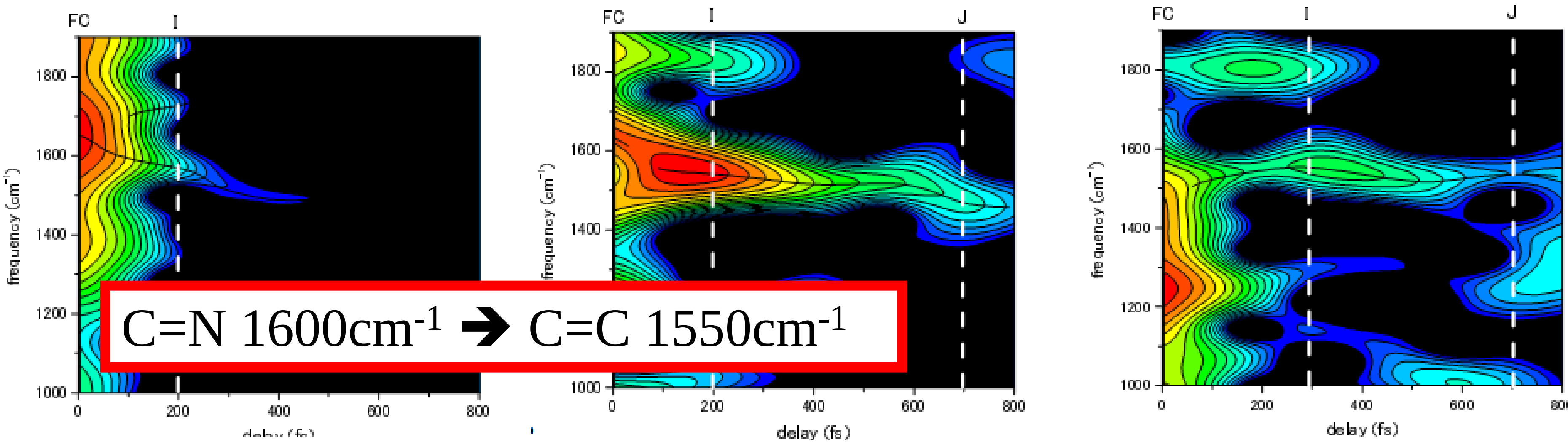
Transient absorption signal (induced absorption, bleaching)

Photo-excitation of G

H-(~200fs)-I-(~500fs)-J-(~3ps)…

Spectrogram analysis
(time-gated Fourier Transform)

real-time observation of molecular vibration frequency



C=N 1600cm^{-1} ➔ C=C 1550cm^{-1}

517nm **577nm** **622nm**

instantaneous frequency of molecular vibration

real-time observation of molecular structure change

G-(hν)-H-(~200fs)-I-(~500fs)-J-(~3ps)...

C=N 1600cm^{-1} ➔ C=C 1500cm^{-1}

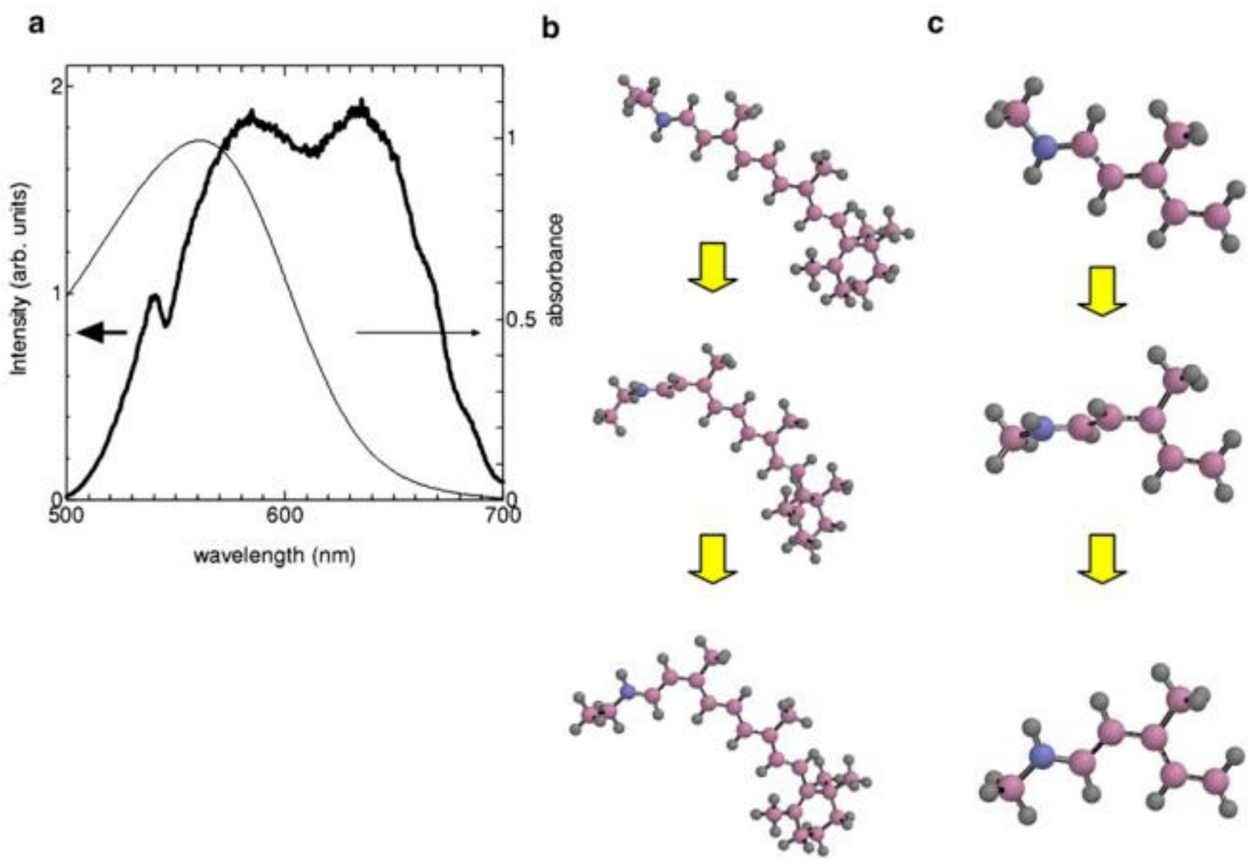


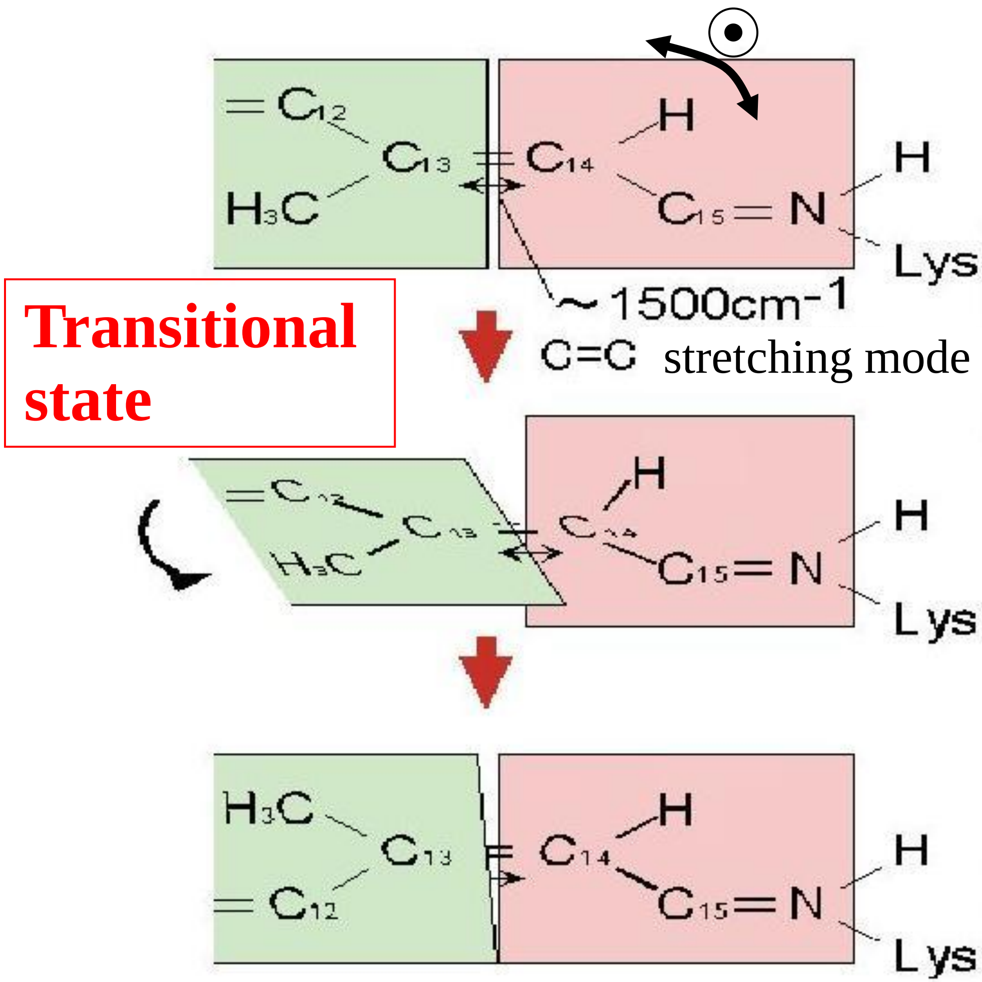
FIGURE 1 Laser spectrum, absorption spectrum of bR, and molecular structure of retinal in bR. (*a*) Laser spectrum (*thick line*) and absorption spectrum of bR (*thin line*). (*b*) Schematic conformational change in the *trans-cis* photoisomerization of the retinal chromophore in bR (CIS/6-31G*//CIS/6-31G*) (1). (*c*) Molecular structures around C_{13}=C_{14} and C_{15}=N clipped out from *b*. In *b* and *c*, purple and blue spheres are carbon and nitrogen atoms, respectively. First, second, and third models in *c* are related to the structures of H, I, and J states, respectively.

Biophysical Journal 96(4) 1447–1461

dynamics of vibrational modes

out-plane & in-plane modes (C=C-H bend)

Dynamics of photoisomerization



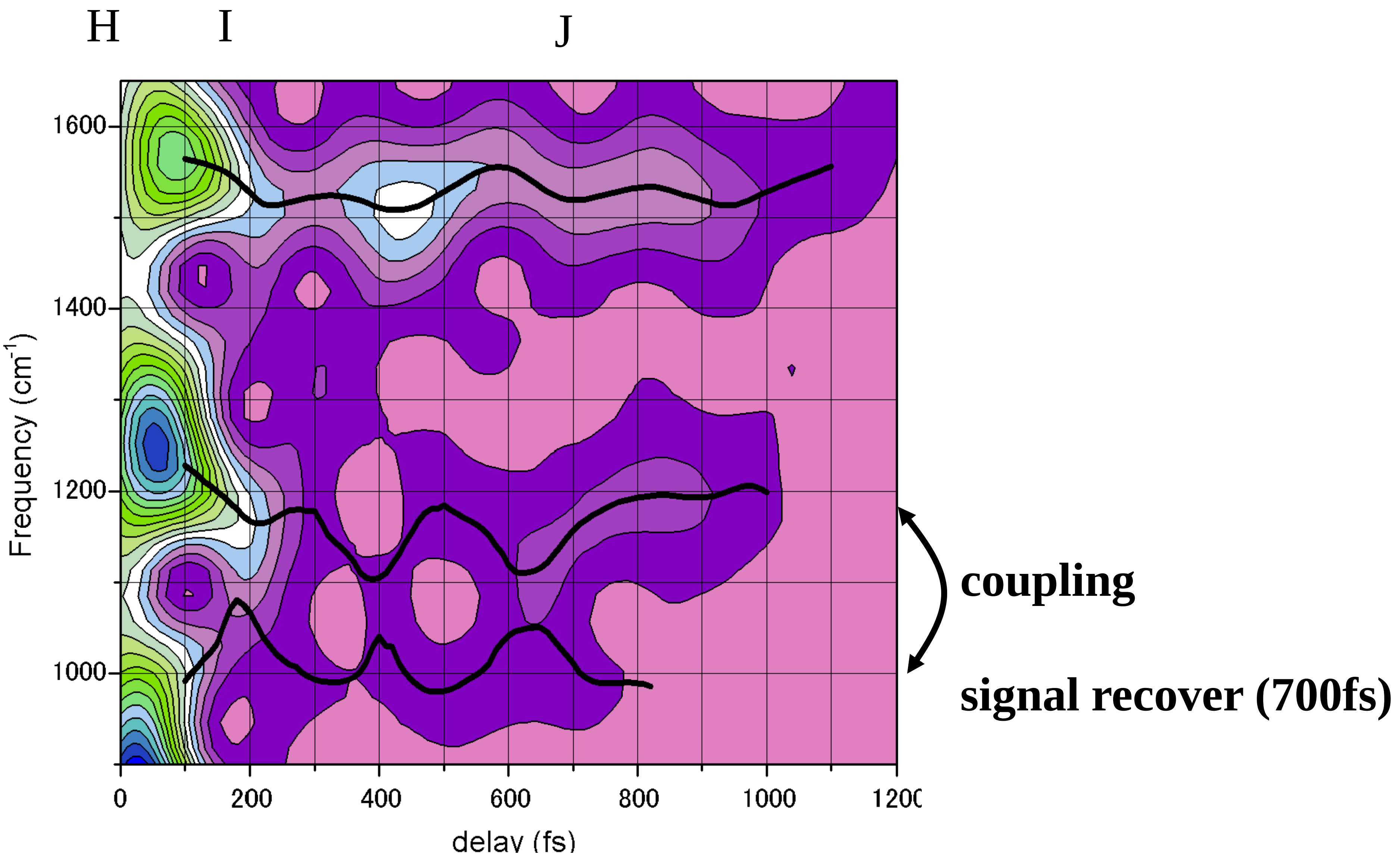
HOOP (hydrogen out of plane)

900-1000cm^{-1}

mix in twist

in-plane C=C-H bending coupling with the C-C stretching

1150-1250cm^{-1}



H
I
J
1600
1400
1200
1000
Frequency (cm-1)
0
200
400
600
800
1000
1200
delay (fs)
coupling
signal recover (700fs)

dynamics of vibrational modes

C=C bond length (C=C stretch)

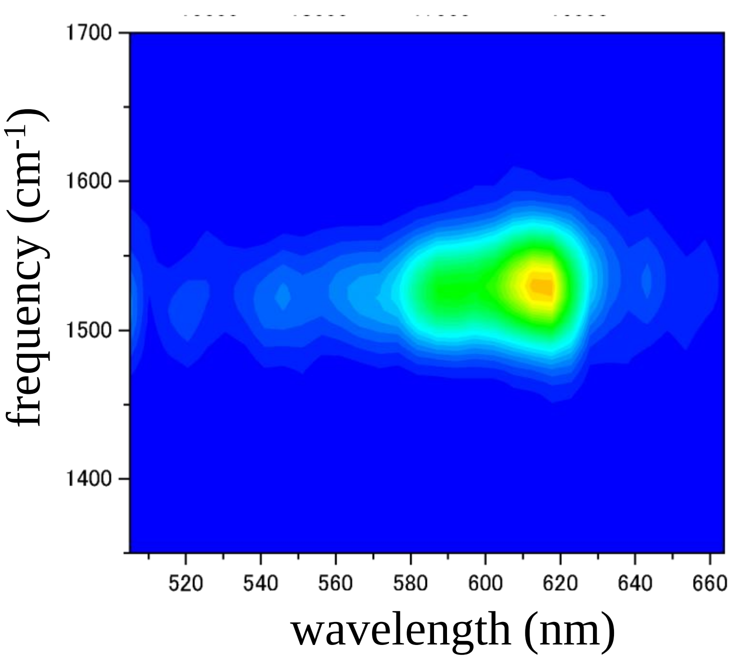
Fourier transform and spectrogram

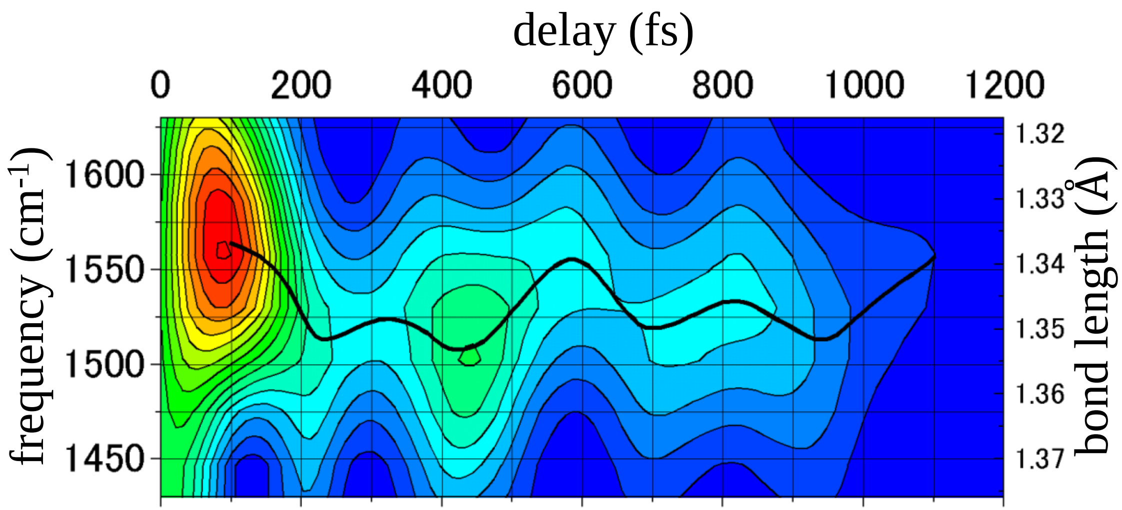
Transient absorption spectrum

FFT

1500cm^{-1}:C=C stretching

spectrogram
(585nm)





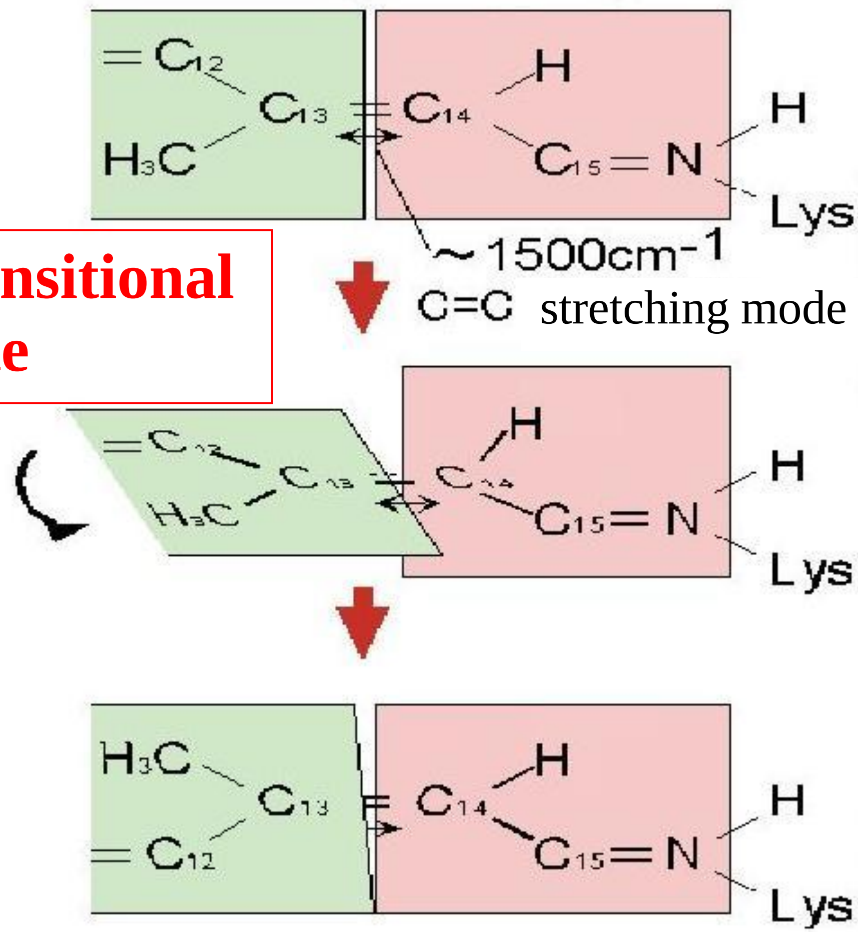
Frequency modulation (200fs-period)

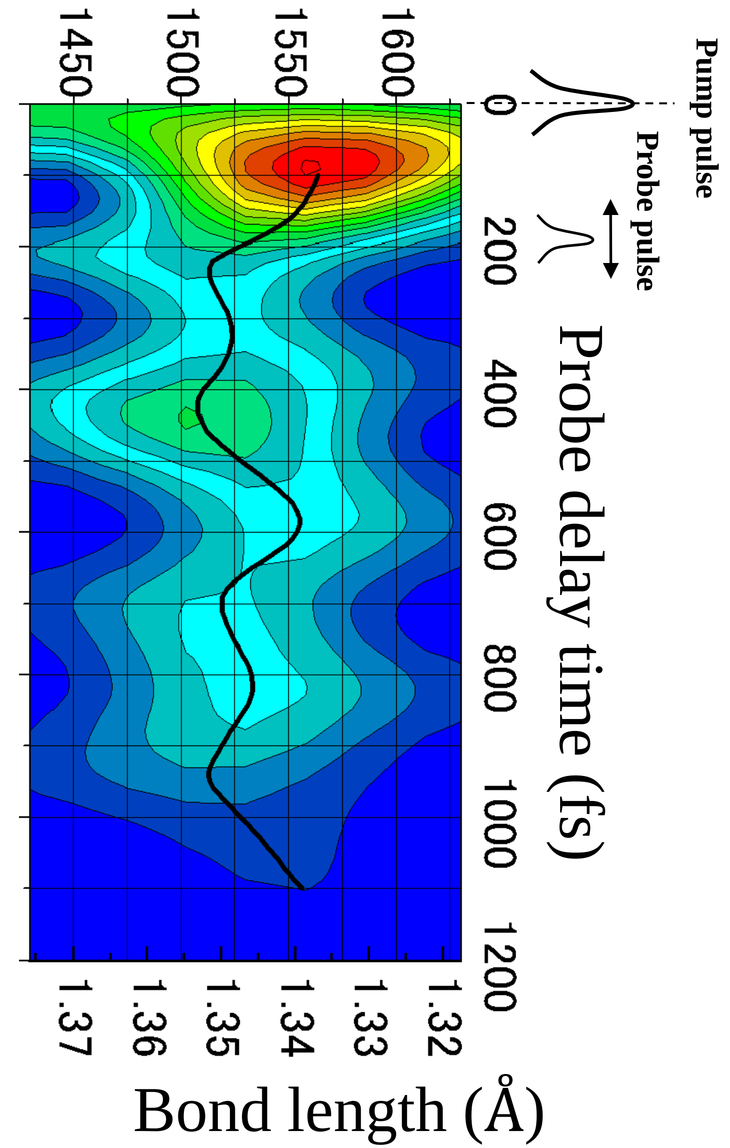
deform of C=C
(bond order and bond length)

Dynamics of photoisomerization

Bond length ⟺ **the instantaneous frequency of molecular vibration**

Transitional state





R. H. Baughman, J. D. Witt, and K. C. Yee, “Raman spectral shifts relevant to electron delocalization in polydiacetylenes”, J. Chem. Phys., 60, 12, 4755-4759 (1974)

$$\nu = C_i\left[a(P+1)(\chi/d)^{3/2}+b\right]^{1/2}$$

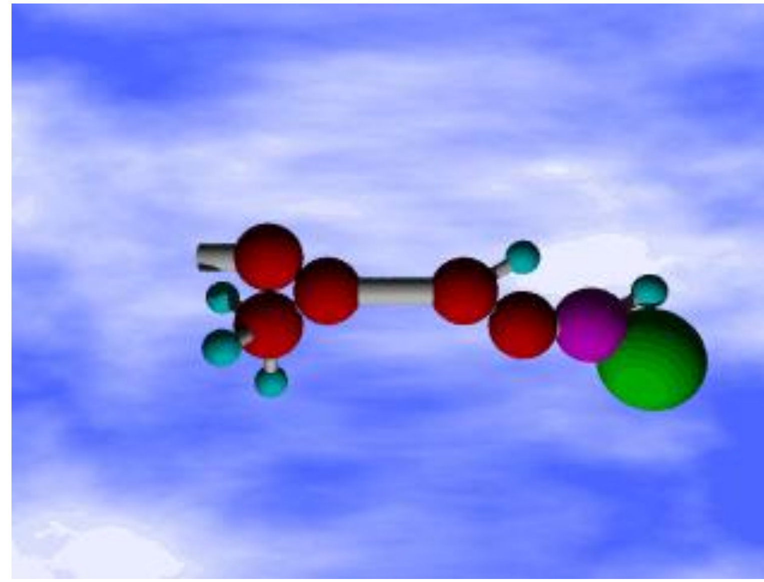
$$a = 1.67\times10^5$$

$$b = 0.30\times10^5$$

$$\chi = 2.5$$

$$C_i = 1.66$$

$$d = 1.489 - 0.151P$$



single bond : $P = \begin{cases} 0 \\ 1 \end{cases}$ $d[\mathring{A}] = \begin{cases} 1.48 \\ 1.33 \end{cases}$ $\nu[cm^{-1}] = \begin{cases} 99 \\ 16 \end{cases}$

double bond :

Gordy’s relationship

$$k = a(P+1)(\chi/d)^{3/2} + b$$

$$d = 1.379 - 0.107P + 0.010P^2$$

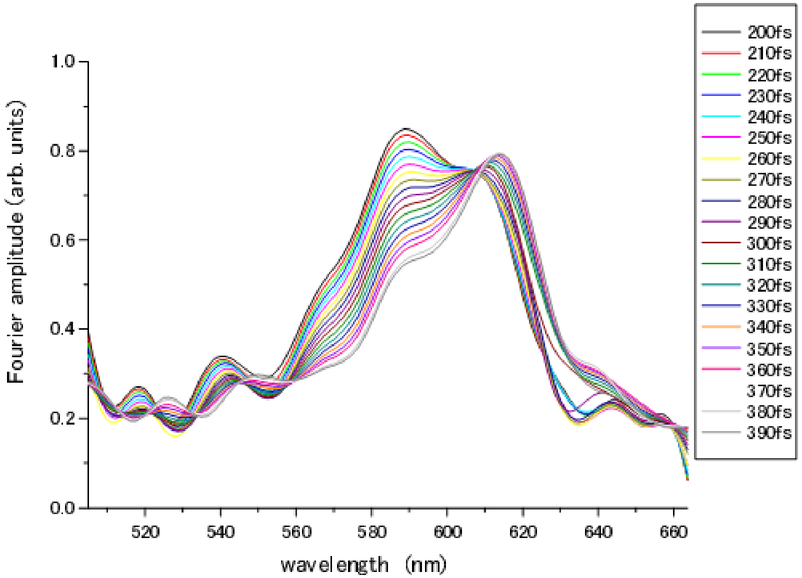
$$d = 1.489 - 0.151P$$

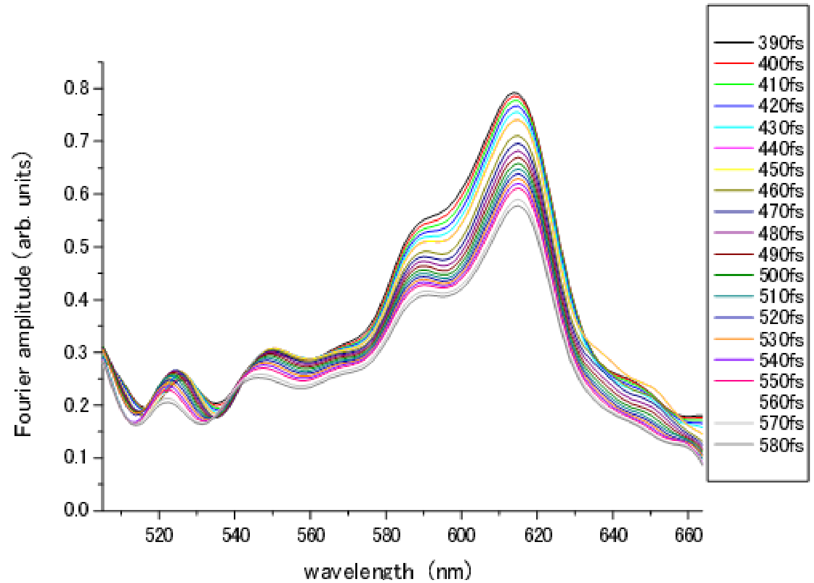
```
solve(1526=1.66*(1.67e5*((1.489-x)/0.151+1)*(2.5/x)^1.5+0.3e5)^0.5,x)
```

4. dynamics of vibrational modes

wavepacket motion, dynamics (C=C stretch)

Fourier amplitude of C=C stretching mode at each delay time (200fs-400fs-600fs)



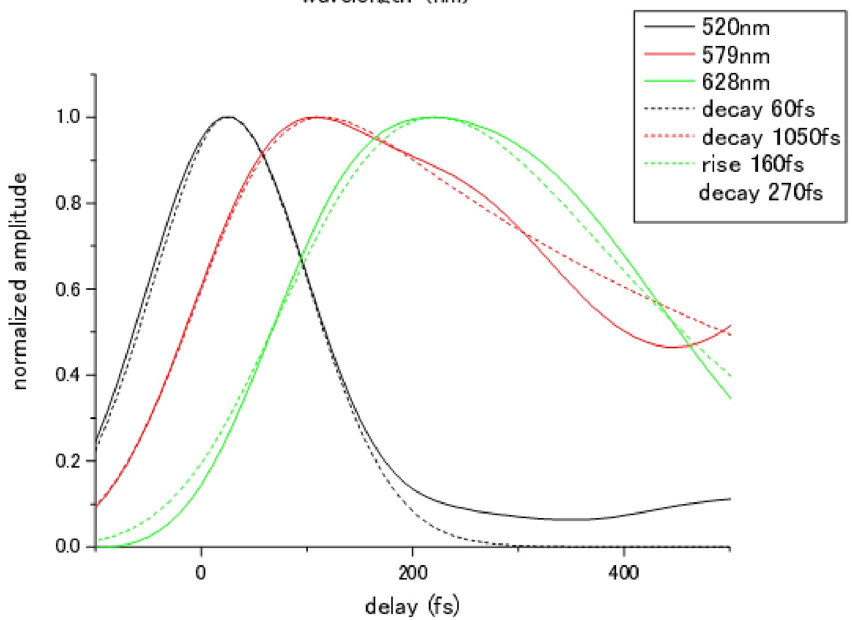


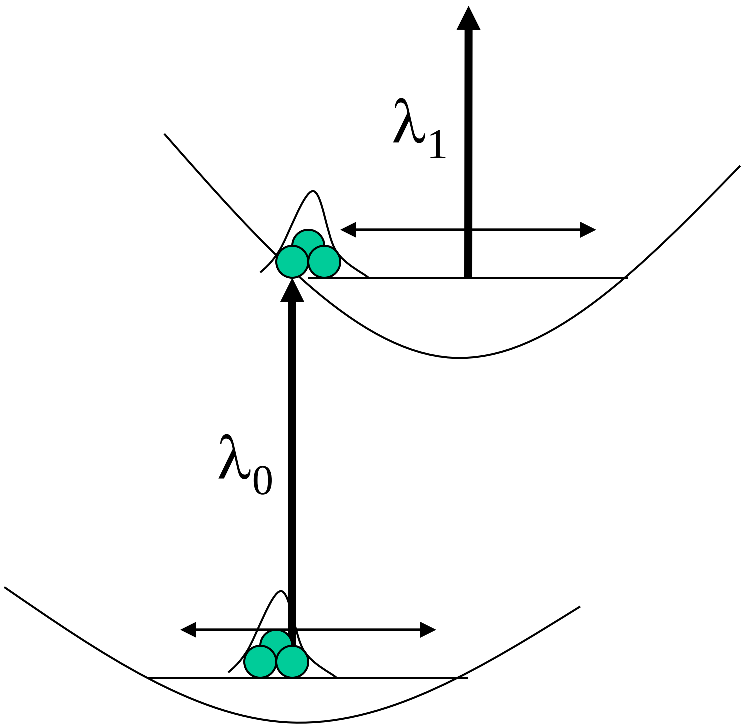
spectrum shift

wavepacket motion

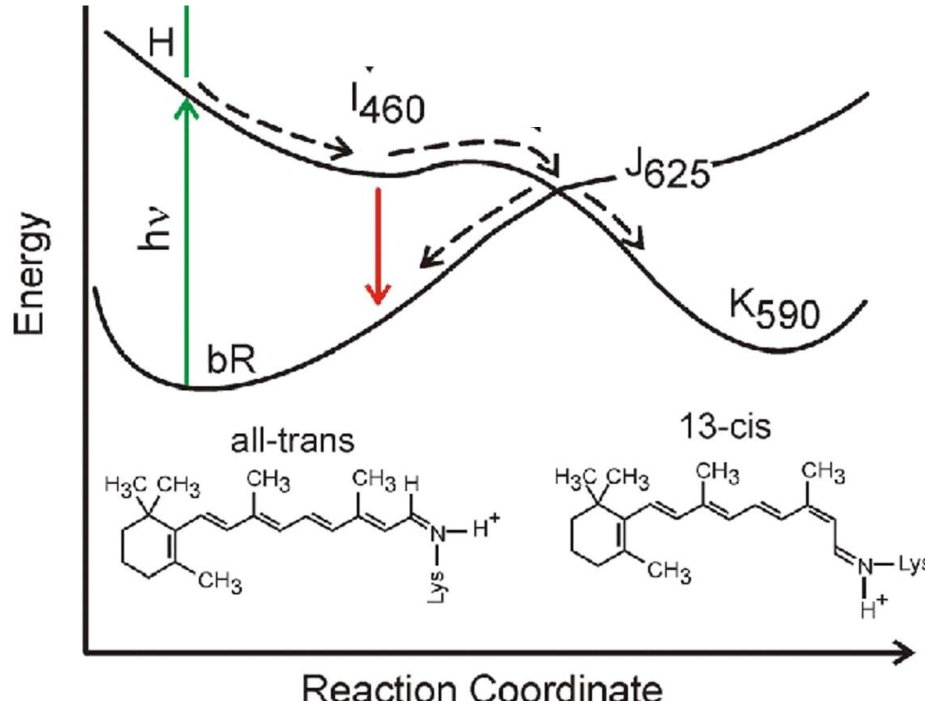
Fourier amplitude trace

dynamics of vib. mode

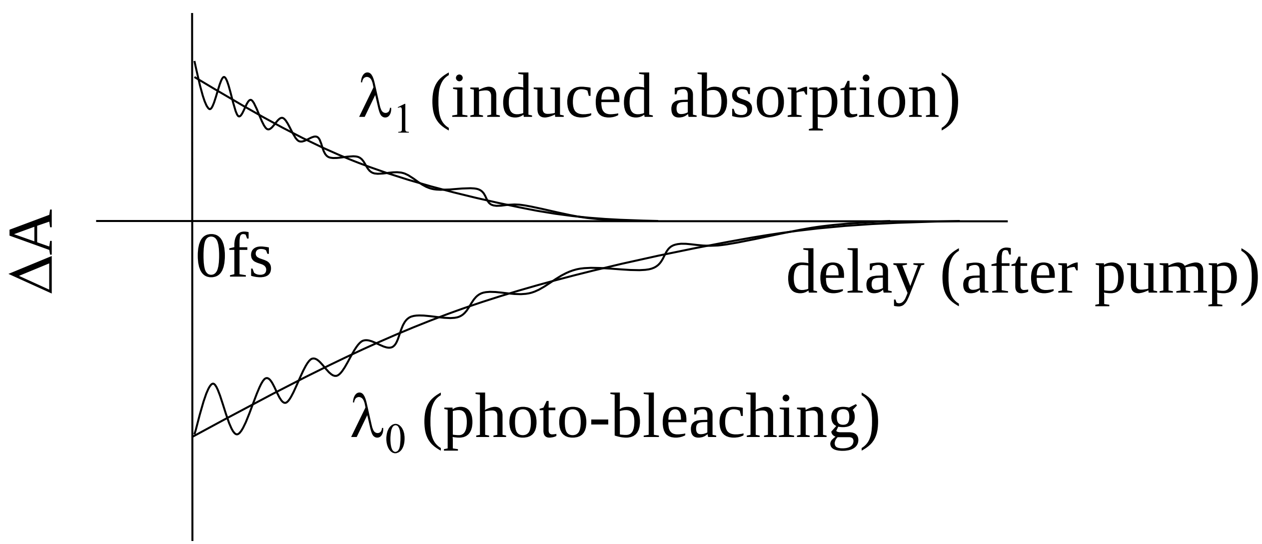




λ_1
λ_0



Energy
H
$h\nu$
I_{460}
J_{625}
K_{590}
bR
all-trans
13-cis
H_3C CH_3
CH_3
CH_3 H
N—H^+
Lys
CH_3
N— Lys
H^+
Reaction Coordinate



λ_1 (induced absorption)
ΔA
0fs
delay (after pump)
λ_0 (photo-bleaching)

conclusion

- ➢Ultrashort laser pulse (sub-10fs, visible)
- ➢bacteriorhodopsin (bR)
  - **Time-resolved absorption spectra (pump-probe)**
  - **Ultrafast dynamics of electronics states**
  - **Ultrafast dynamics of vibrational modes**
- ➢out-plane & in-plane modes (C=C-H bend)
- ➢C=C bond length (C=C stretch)
- ➢Wavepacket motion, Dynamics (C=C stretch)

Thank you for your kind attention

Topics not shown today

Quantum information
entangled photon pair beam
high efficiency generation

ultrafast spectroscopy of various materials
P3HT: polymer solar cell
dynamics of electron after photoexcitation

DR19 : laser dye
large dipole moment (for hologram, etc)
in film / in solution

hemoglobin : $HbO_2 \Leftrightarrow Hb$