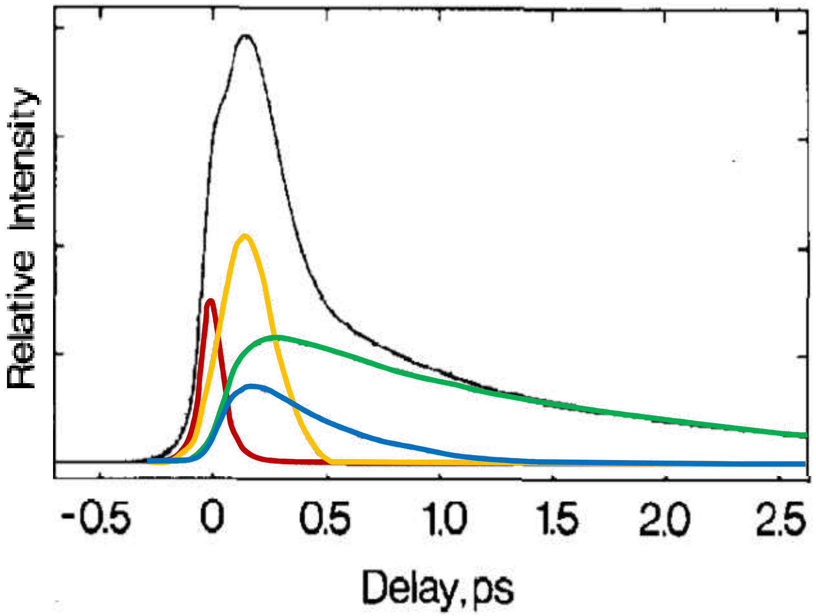
Analysis of the Optical Heterodyne Detected-Optical Kerr Effect(OHD-OKE) signal

(Temporal Analysis)

2010 5 15 Jun Hee Sun

OHD-OKE signal

- CS2 Kerr signal (laser pulse FWHM:65fs)



- OHD-OKE signal $S(\tau)$

$$S(\tau) \propto \int_{-\infty}^{\infty} G_0^{(2)} R(t-\tau) dt$$

$G_0^{(2)}$:laser pulse autocorrelation

$R(t)$: impulse response of the induced birefringence

$$R(t) = \sigma(t) + \sum_i A_i r_i(t)$$

$r(t)$: nuclear response

$\sigma(t)$: electronic response

$$\sigma(t) = A_0 \delta(t)$$

$$r_1(t) = A_1 \exp(-\frac{t}{\tau_{diff}})[1-\exp(-\frac{2t}{\beta_1})]$$

$$r_2(t) = A_2 \exp(-\frac{t}{\tau_{\text{int}}})[1-\exp(-\frac{2t}{\beta_2})]$$

$$r_3(t) = A_3 \exp(-\frac{t}{\tau_{lib}}) \exp(-\frac{\Delta^2 t^2}{2}) \sin(\omega_0 t)$$

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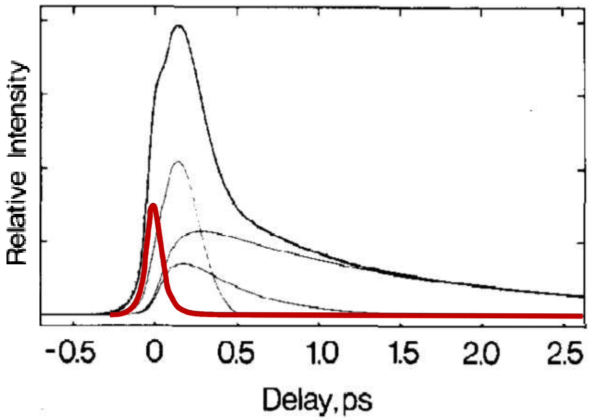
OHD-OKE response function

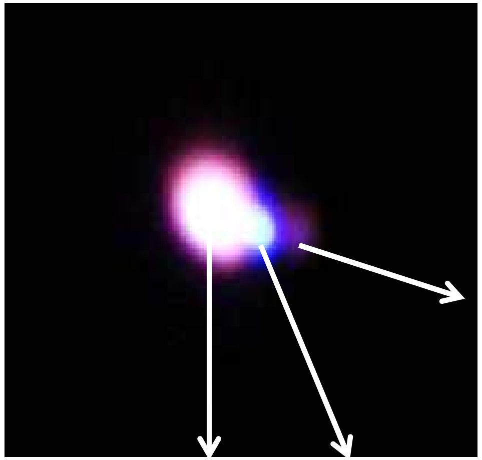
Ⅰ. Instantaneous electronic response $\sigma(t)$



- Gaussian function

$$G_0^{(2)}(t) = \frac{A}{w\sqrt{\pi/2}} \exp\left(-\frac{2(t-t_0)^2}{w^2}\right)$$

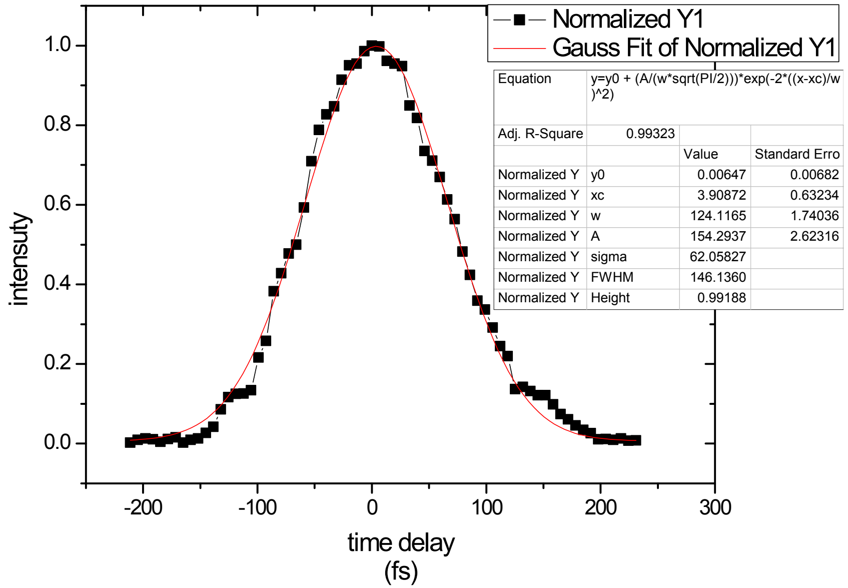
Autocorrelation

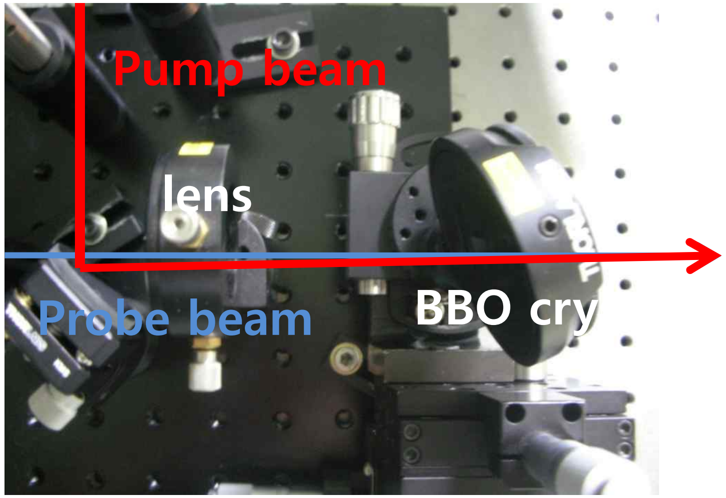


Probe beam

Pump beam

Autocorrelation 400nm





- ✓ **FWHM** : 146fs
- ✓ **pulse width** :

$$\frac{\Delta t_{pulse}}{\Delta t_{autocorrelation}} = 0.707$$

146fs X 0.707 = **103fs**

OHD-OKE response function

Ⅱ. Diffusive reorientational

$$r_1(t) = A_1 \exp(-\frac{t}{\tau_{diff}})[1-\exp(-\frac{2t}{\beta_1})]$$

Ⅲ. Intermediate contribution

$$r_2(t) = A_2 \exp(-\frac{t}{\tau_{\text{int}}})[1-\exp(-\frac{2t}{\beta_2})]$$

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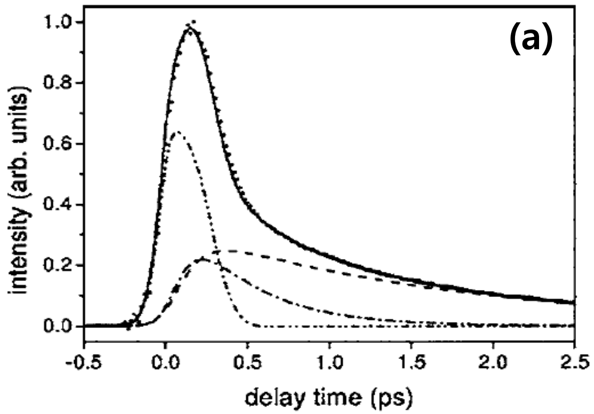
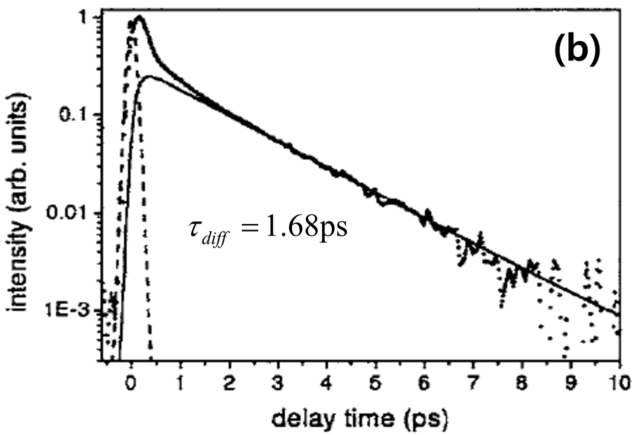
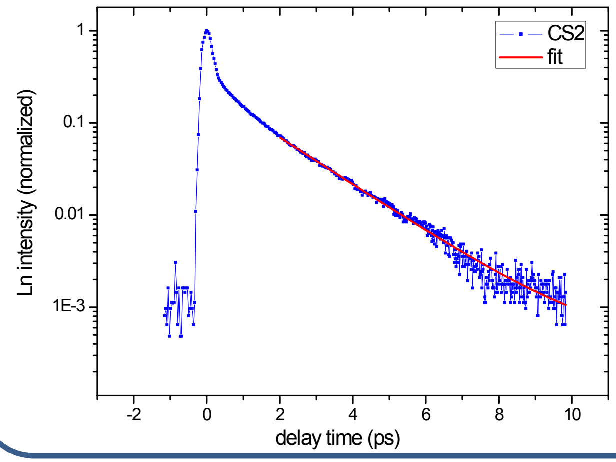




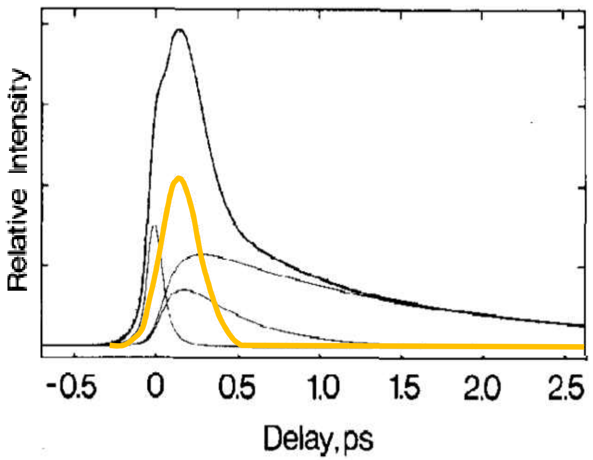
OHD-OKE signal for neat CS2 **(a)** short-time scan at 293K (circles) together with the fitted components : libration (dash dot dot), intermediate(dash dot), diffusive(dash), Complete fit(solid line) **(b)** long-time scan showing the fitted Diffusive component (solid line) and the autocorrelation (dash)

- **Our data :** $\tau_{diff} = 1.69\text{ps}$



OHD-OKE response function

Ⅳ . Intermolecular Libration motion



$$r_3(t) = A_3 \exp(-\frac{t}{\tau_{lib}}) \exp(-\frac{\Delta^2 t^2}{2}) \sin(\omega_0 t)$$

τ_2 : dephasing time

α : inhomogeneous depehasing rate

$\frac{\omega_0}{2\pi}$: center frequency

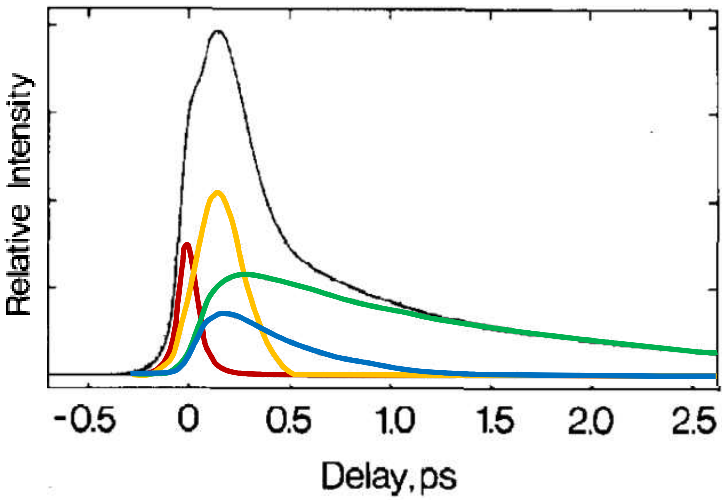
※ Rman resonant ex) CS_2

$$\nu_0 = \frac{\omega_0}{2\pi c}$$

$$35.4 / cm = \frac{\omega_0}{2\pi \times 3.14}$$

$$\therefore \omega_0 = 6.67 / ps$$

OHD-OKE fitting example



- fwhm :65fs (633nm)
- sample : CS2

Volume fraction CS_2	η [a] (cP)	ρ [a] (g/cm^3)	Electronic response A_1 [b]	Librational response A_2	ω_0 [c] (ps^{-1})	$\bar{\nu}_0$ [c] (cm^{-1})	$2\pi/\omega_0$ [d] (ps)	τ_2 [c] (fs)	α (ps^{-1})	$\Delta\bar{\nu}_I$ [f] (cm^{-1})	Intermediate contribution A_3	τ_3 (fs)	β_3 [g] (fs)	Orientional anisotropy A_4	τ_4 [h] (ps)	β_4 [g] (fs)
1.0	0.366	1.262	0.27	0.39	6.67	35.4	0.94	400	4.44	55.3	0.14	400	150	0.20	1.61	150

- $A_1 + A_2 + A_3 + A_4 = 1$
- $\Delta\nu = \dfrac{\omega_0}{2\pi c}$; The temporal profile of the librational response and its corresponding spectral distribution are determined by both the parameter α and ω_0.
- $\dfrac{2\pi}{\omega_0}$; period of oscillation
- $\Delta\nu_I = \dfrac{\alpha(2\ln 2)^{1/2}}{\pi c}$; fwhm of inhomogeneous distribution
- $\beta_3 = \beta_4 = \dfrac{1}{\omega_0}$

Chem. Phys. Lett. 150, 138 (1988)

Reference paper

- Chem.Phys.Lett.1988.150.138
- EEEJ.Quantum Electron.QE-24(1988)443
- J.Chem.Phys.123.05409.2005