

## Optical Heterodyne Detected Optical Kerr Effect (OHD OKE) response

IEEE J. Quantum Electron. QE-24 (1988) 443

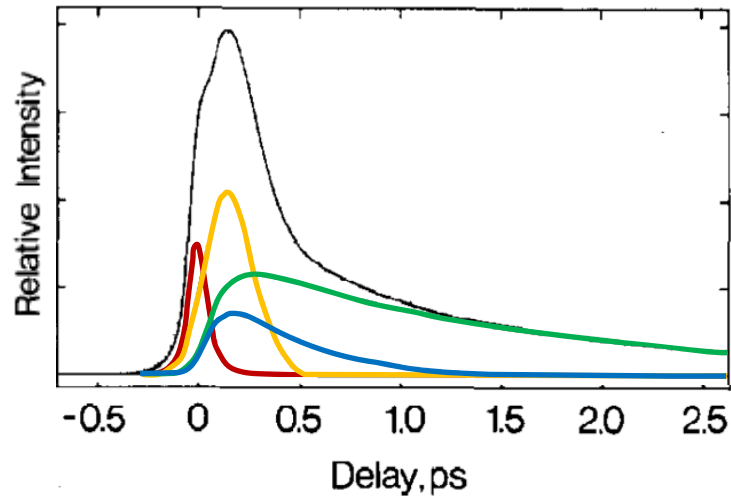
Chem. Phys. Lett. 150, 138 (1988)

IEEE J. Quantum Electron. QE-2 (1996) 756

J. Chem. Phys. 123, 054509 (2005)

# OHD OKE response

CS2 Kerr signal (FWHM:65fs)



## ◆ OHD-OKE signal $T(\tau)$

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

$G_0^{(2)}$ : laser pulse autocorrelation  
 $R(t)$ : impulse response of the induced birefringence

$$T(\tau) = \int_{-\infty}^{\infty} I_{probe}(t-\tau) \{1 + \sin[\phi(t)]\} dt$$

$$\phi(t) = \left(\frac{n_{xx}\omega}{c} L - \omega t\right) - \left(\frac{n_{yy}\omega}{c} L - \omega t\right) = \frac{\omega L}{c} \Delta n(t)$$

$$\Delta n(t) = \sum_m n_m(t) = \sum_m \int_{-\infty}^{\infty} I_{pump}(t') r_m(t-t') dt'$$

## ◆ Response function $R(t)$

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

$\sigma(t)$ : purely electronic hypolarizability

pump, probe pulses are temporally as well as spatially overlapped

$r(t)$ : inter- and intra- nuclear contributions

i)  $r_2(t)$

**Coherently excited intermolecular librational motion**

<http://www.mbi-berlin.de/en/research/projects/2-04/highlights/MolStructDynamics-2005.html>

# OHD OKE response

The impulse response function for the orientational motion of an ensemble of molecules, each in an identical, locally harmonic potential,

$$r_{2i}(\omega_i, t) = \left( \frac{n_2^i \mu_i^{1/2}}{\omega_i I^{1/2}} \right) \times \exp\left(-\frac{t}{\tau_{2i}}\right) \sin(\omega_i t)$$

For an inhomogeneously broadened transition the coherent vibrational amplitude is given by a superposition of the different frequency components.

$$r_2(t) = \sum_i B(\omega_i) \sin(\omega_i t) \exp\left(-\frac{t}{\tau_2}\right)$$

$$r_2(t) = \exp\left(-\frac{t}{\tau_2}\right) \int_0^\infty B(\omega) \sin(\omega t) d\omega$$

$$r_2(t) \approx A_2 \exp\left(-\frac{t}{\tau_2}\right) \exp\left(-\frac{1}{2} \alpha^2 t^2\right) \sin(\omega_0 t)$$

$\tau_2$  : dephasing time

$\alpha$  : inhomogeneous dephasing rate

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

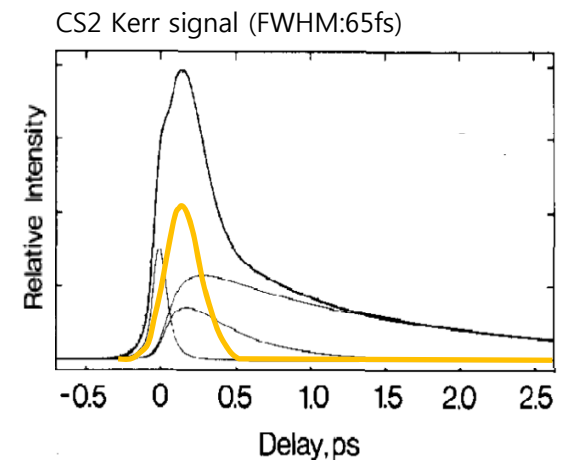
## ※ Rman resonant

ex) CS<sub>2</sub>

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

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

$$\therefore \omega_0 = 6.67 / \text{ps}$$



# OHD OKE response

ii)  $r_3(t)$

**Intermediate contribution**

<http://www.mbi-berlin.de/en/research/projects/2-04/highlights/MolStructDynamics-2005.html>

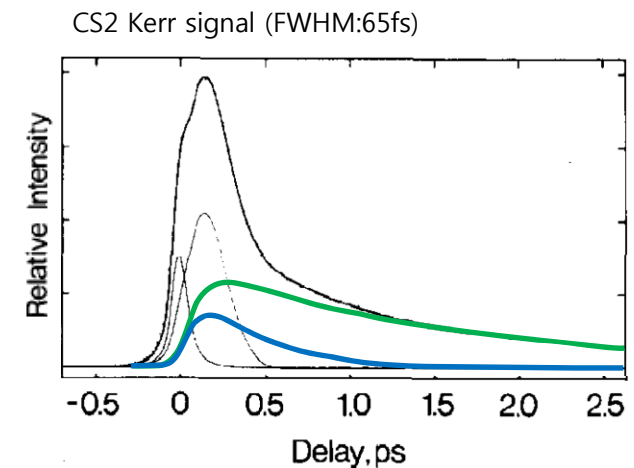
Interaction between the dipoles induced in the medium molecules by the strong incident field

iii)  $r_4(t)$

**Diffusive reorientational**

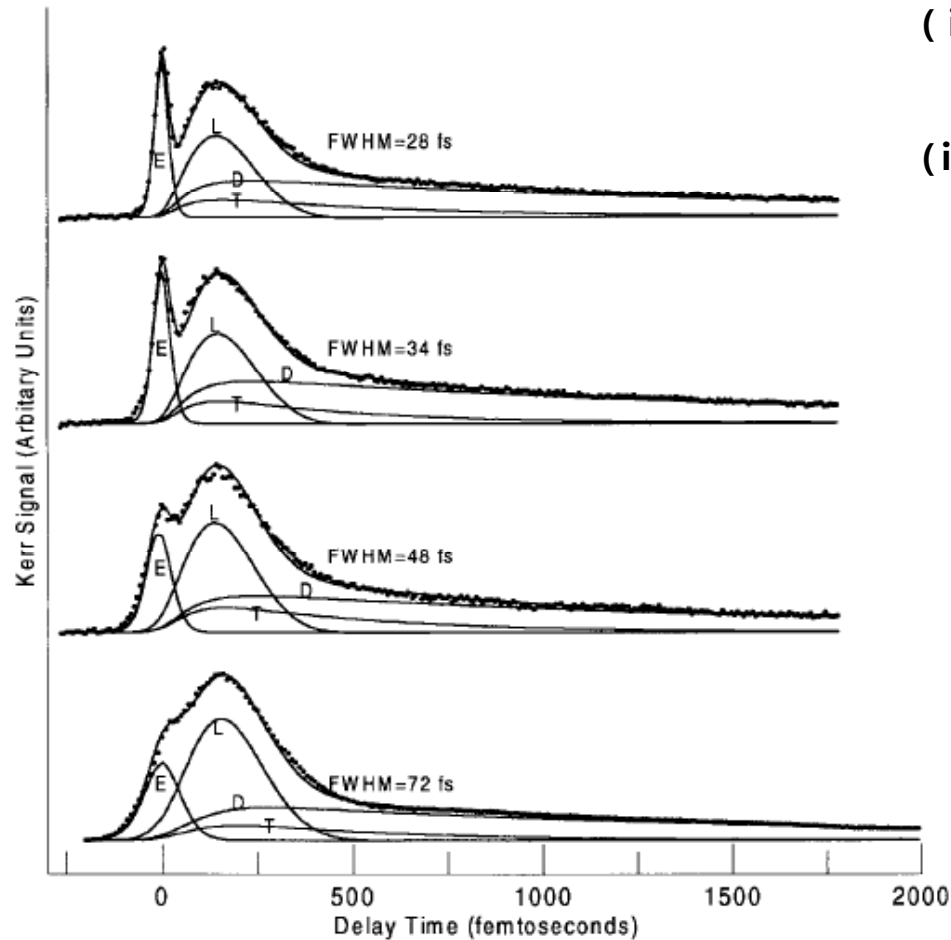
$$r_i(t) = A_i \exp\left(-\frac{t}{\tau_i}\right) \left[1 - \exp\left(-\frac{2t}{\beta_i}\right)\right]$$

$$\beta = \frac{1}{\omega_0}$$



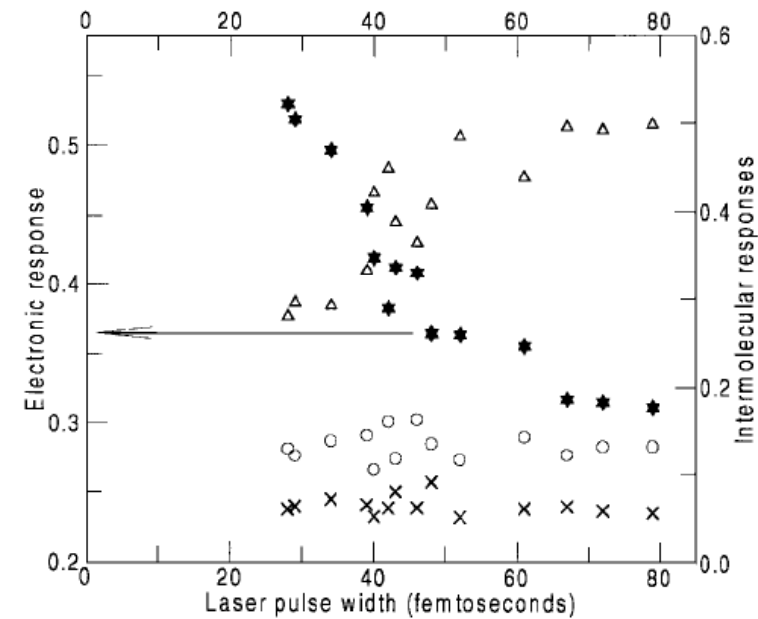
# OHD OKE response

- ◆ Variation of the transient OHD-OKE profile of liquid CS<sub>2</sub> as a result of changing the incident laser pulsewidth(FWHM)



electronic(E), nuclear(L, D, T)

- (i) Creates some net alignment of the molecules, giving rise to an **orientational anisotropy**
- (ii) produces an ensemble molecules **coherently librating in local intermolecular potentials**

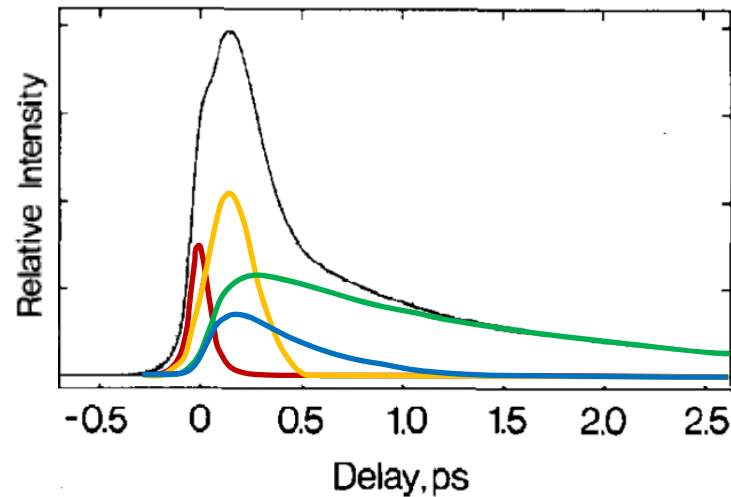


electronic(★),

libration(△), diffusive reorientation(○),  
polarizability distortion(×)

# OHD OKE response

CS<sub>2</sub> Kerr signal (FWHM:65fs)



Volume fraction CS <sub>2</sub>	$\eta^{a)}$ (cP)	$\rho^{a)}$ (g/cm <sup>3</sup> )	Electronic response $A_1^{b)}$	Librational response							Intermediate contribution			Orientational anisotropy		
				$A_2$	$\omega_0^{c)}$ (ps <sup>-1</sup> )	$\bar{\nu}_0^{c)}$ (cm <sup>-1</sup> )	$2\pi/\omega_0^{d)}$ (ps)	$\tau_2^{e)}$ (fs)	$\alpha$ (ps <sup>-1</sup> )	$\Delta\bar{\nu}_l^{f)}$ (cm <sup>-1</sup> )	$A_3$	$\tau_3$ (fs)	$\beta_3^{g)}$ (fs)	$A_4$	$\tau_4^{h)}$ (ps)	$\beta_4^{k)}$ (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

<sup>a)</sup> Measured at 295 ± 0.1 K; error ± 0.002 for each. <sup>b)</sup> Error in all amplitudes ± 5%;  $A_1 + A_2 + A_3 + A_4 = 1$ .

<sup>c)</sup>  $\bar{\nu}_0 = \omega_0 / 2\pi c$ ; error in  $\omega_0$  + 5%, -40%. The temporal profile of the librational response and its corresponding spectral distribution are determined by both the parameters  $\alpha$  and  $\omega_0$  (or  $\Delta\bar{\nu}_l$  and  $\bar{\nu}_0$ ). The rapid decay of this signal, however, makes it difficult to identify a unique value for either parameter in the current analysis. For neat CS<sub>2</sub> a frequency domain stimulated Raman gain experiment [16] has unambiguously identified a low-frequency, spectrally broad Raman band centered at 35 cm<sup>-1</sup>, apparently corresponding to the librational response observed here and allowing us to fix this parameter in the current analysis. For the other solutions, the values reported in this table correspond to the maximum frequency (and corresponding minimum inhomogeneous bandwidth) that will adequately describe the data. Thus, the shifts in  $\omega_0$  on dilution evident in this table represent a lower limit for this effect.

<sup>d)</sup> Period of oscillation. <sup>e)</sup>  $\tau_2$  fixed at the value of  $\tau_3$ , error ± 50 fs. <sup>f)</sup>  $\Delta\bar{\nu}_l = \alpha(2 \ln 2)^{1/2} / \pi c$ , fwhm of inhomogeneous distribution; error + 15%, -3%.

<sup>g)</sup>  $\beta_3 = \beta_4 = 1/\omega_0$ . <sup>h)</sup> Errors in orientational decays: neat CS<sub>2</sub>, ± 0.05 ps; 75%, ± 0.1 ps; 50%, ± 0.15 ps; 25%, 20%, ± 0.2 ps.

