

Optical Kerr Effect Spectroscopy of Simple Liquids

Qin Zhong , John T. Fourkas

In this paper, we review the state of the field of optical Kerr effect (OKE) spectroscopy of simple liquids, with a focus on results from our laboratory. We discuss the history and the theoretical underpinnings of this technique. We consider contemporary issues in the interpretation of OKE spectra, including the origin of the “intermediate” response and the factors affecting the shape of the reduced spectral density. We highlight some applications of the OKE spectroscopy of simple liquids, including the study of liquid mixtures and the behavior of liquids in nanoconfinement. We also discuss future prospects for OKE spectroscopy and related techniques.

1. Experimental Geometry and Signal

Optical Heterodyne Detected – Optical Kerr Effect (OHD-OKE)

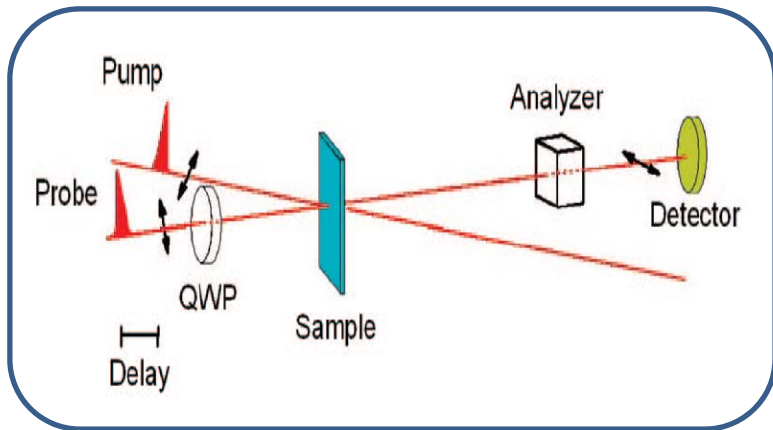


Figure 1. Schematic layout for a polarization spectroscopy implementation of the optical Kerr effect. The pump pulse is polarized at 45° , and the probe pulse is polarized vertically. The analyzer polarizer is set to pass horizontally polarized light, and the leakage is measured as a function of delay between the pump and probe pulses. To implement optical heterodyne detection, a quarter-wave plate (QWP) is placed after the first polarizer in the probe beam.

Polarization :

pump and probe : $\nless 45^\circ$

probe and analyzer : \perp

QWP and probe : $\parallel + 1^\circ$

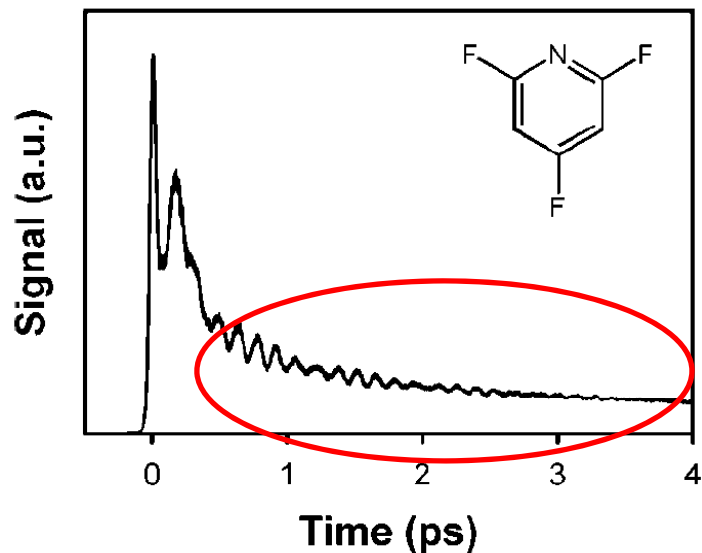
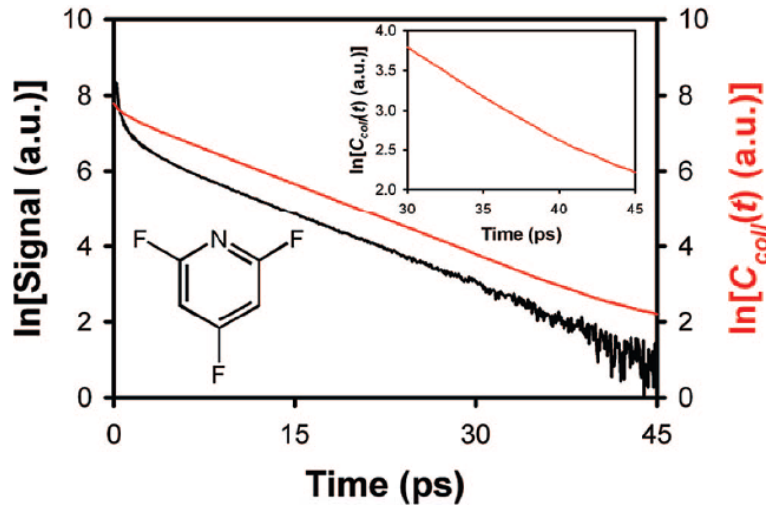


Figure 2. A typical OKE decay, in this case for 2,4,6-trifluoropyridine at 306 K. The sharp feature at zero delay time is the electronic response. The oscillations arise from Raman-active intramolecular vibrational modes. Coherently excited intermolecular modes contribute significantly to the decay for more than a picosecond, and orientational diffusion dominates at longer times.

- 2,4,6-trifluoropyridine at 306K
- Delay zero : electronic response
- Oscillation : Raman-active intramolecular vibrational modes

The OKE response can be integrated to determine $C_{\text{coll}}(t)$ directly



collective orientational decay time :

$$\tau_{\text{coll}} = \frac{g_2}{j_2} \tau_{\text{sm}}$$

τ_{sm} : single molecule orientational correlation time

g_2 : static pair orientational correlation parameter

j_2 : dynamic pair orientational correlation parameter

- g_2 depends upon the degree of parallel ordering in a liquid
- generally assumed that j_2 is unity in simple liquid

Figure 3. Comparison of the OKE decay (black) and $C_{\text{coll}}(t)$ derived by integrating the OKE decay (red) for 2,4,6-trifluoropyridine at 306 K. From the magnified portion of $C_{\text{coll}}(t)$ shown in the inset, it is apparent that the integrated data begin to exhibit low-frequency noise and deviation from linearity at a time of about 35 ps. This is the cutoff time that was chosen in fitting the correlation function.

2. Fourier-Transform Deconvolution

The OKE signal $S(t)$: $S \propto [I_{\text{pump}} \otimes I_{\text{probe}}] \otimes R_{xyxy}^{(3)}$

Second-harmonic generation cross-correlation between pump and probe :

$$G^{(2)}(t) = \int_{-\infty}^{\infty} I_{\text{pump}}(t') I_{\text{probe}}(t-t') dt'$$

Fourier transform : $F[G^{(2)}(t) \otimes R_{xyxy}^{(3)}(t)] = F[G^{(2)}(t)] \otimes F[R_{xyxy}^{(3)}(t)]$

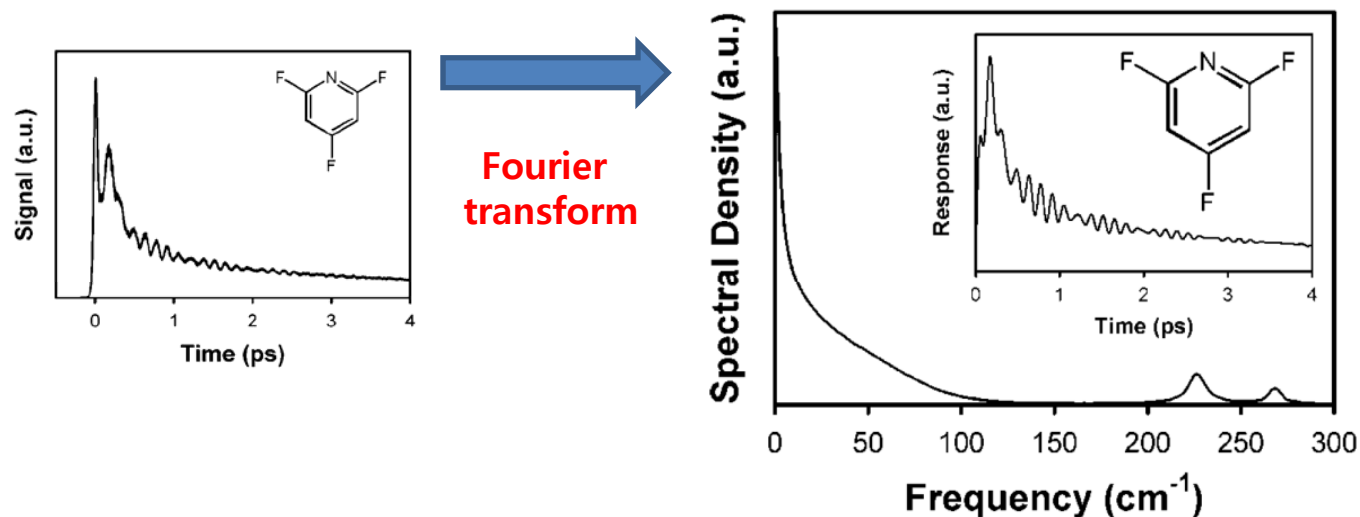


Figure 4. Spectral density for 2,4,6-trifluoropyridine at 306 K. The peaks near 230 and 270 cm⁻¹ arise from intramolecular vibrations. Shown in the inset is the deconvoluted nuclear response function for this liquid. Note that the electronic response is no longer present after deconvolution.

3. Microscopic Origin of the Intermolecular Portion of the OKE Signal

Reduced spectral density (**RSD**) : remove the diffusive orientational portion of the spectral density to obtain

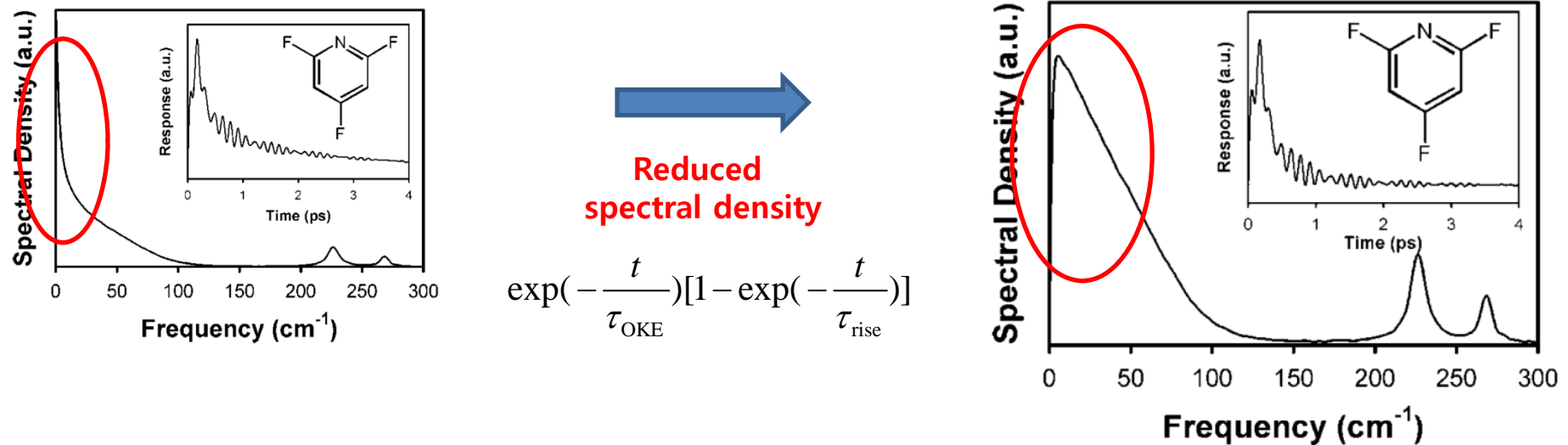
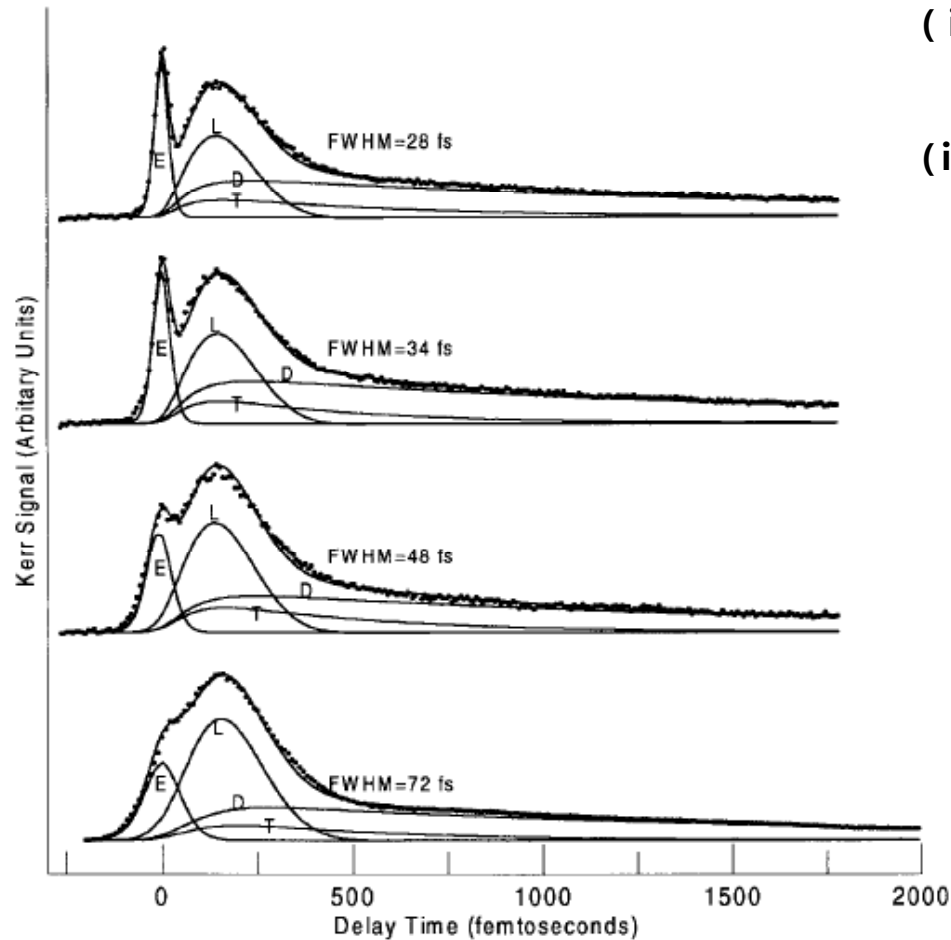


Figure 5. Reduced spectral density for 2,4,6-trifluoropyridine at 306 K. This is an example of a “triangular” RSD typical of fluorinated aromatics. Shown in the inset is the nuclear response function without the contribution from orientational diffusion. Once the contribution from intermolecular modes has decayed completely, any remaining contributions from intramolecular modes oscillate about zero.

- rise time t_{rise} is generally to be 200fs or less

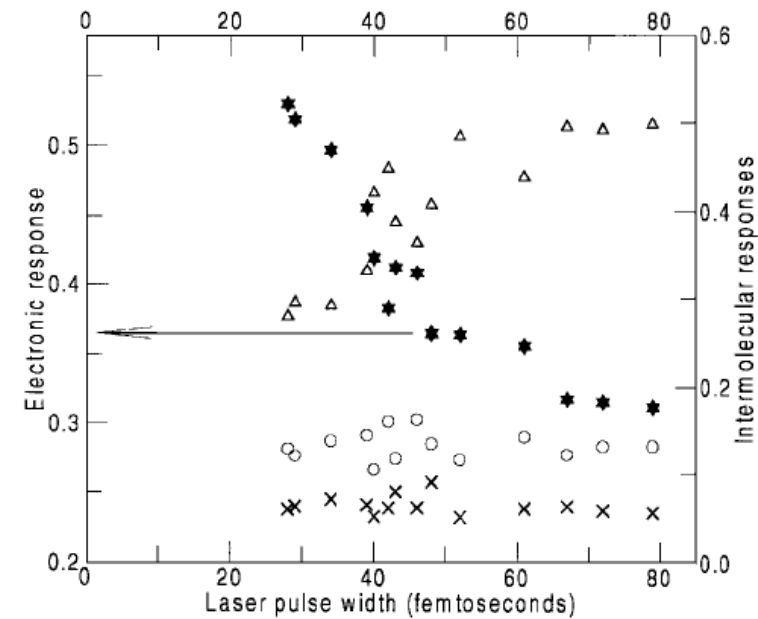
Example 1 : IEEE J. Quantum Electron. QE-2 (1996) 756

- Variation of the transient OHD-OKE profile of liquid CS₂ 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(×)

Example 2 : J.Chem.Phys,123,054509,2005

Time-resolved optical Kerr-effect investigation on CS₂/polystyrene mixtures

Ismael A. Heisler,^{a)} Ricardo R. B. Correia, Tiago Backup, and Silvio L. S. Cunha

Nádyá P. da Silveira

$$I(t) \propto \int_{-\infty}^{\infty} dt A_c(t) R(t - \tau)$$

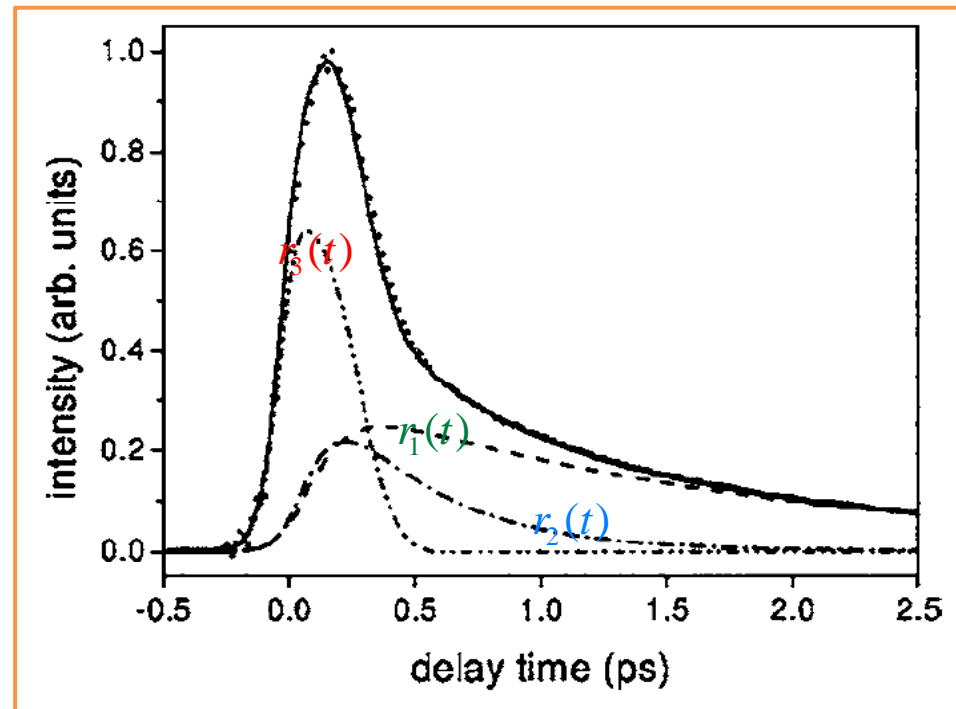
$$= A_c(t) \otimes R(t) = A_c(t) \otimes [\sigma(t) + r(t)]$$

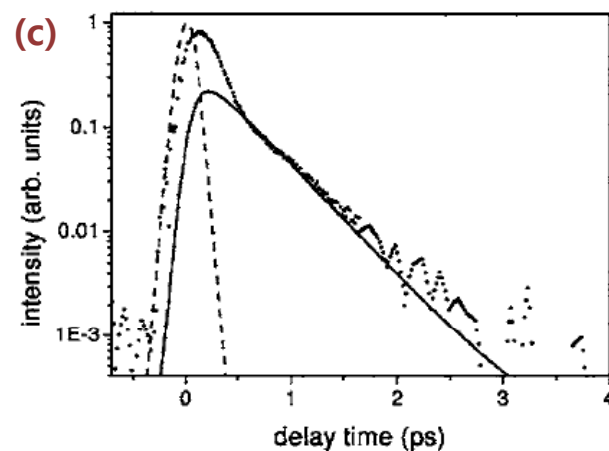
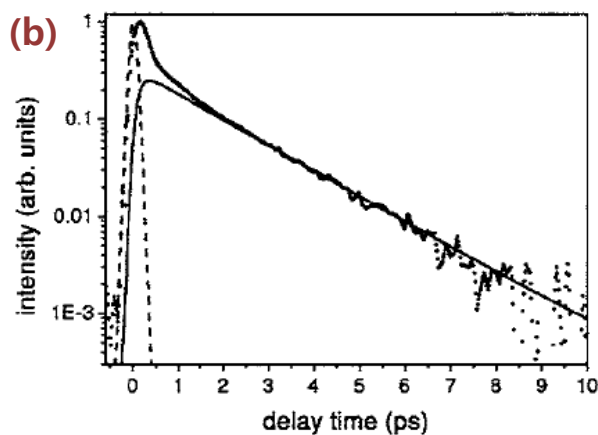
$$r_1(t) = a_1 \exp\left(-\frac{t}{\tau_{\text{diff}}}\right) \left(1 - \exp\left(-\frac{t}{\tau_{\text{rise1}}}\right)\right)$$

$$r_2(t) = a_2 \exp\left(-\frac{t}{\tau_{\text{int}}}\right) \left(1 - \exp\left(-\frac{t}{\tau_{\text{rise2}}}\right)\right)$$

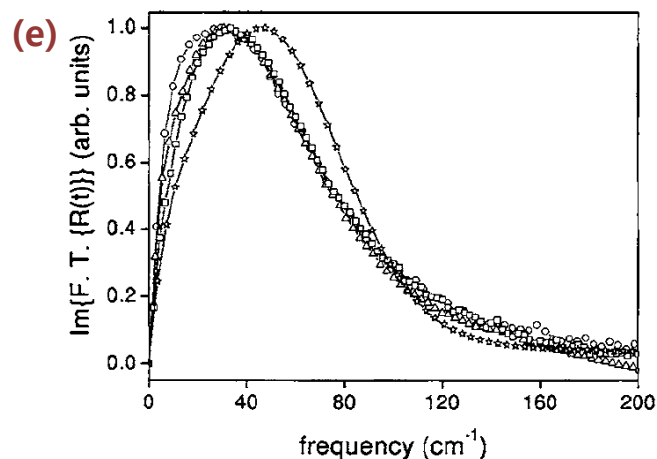
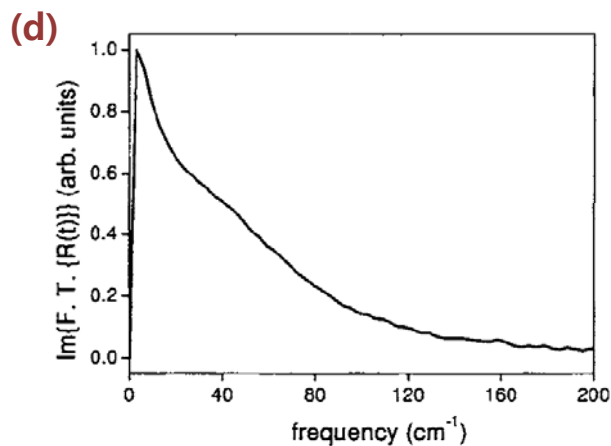
$$r_3(t) = a_3 \exp\left(-\frac{\alpha^2 t^2}{2}\right) \sin(\omega_0 t)$$

% by wt of PS in the mixture	0
a_1^a	0.17
$\tau_{\text{dif}} \text{ (ps)}^b$	1.68
a_2	0.28
$\tau_{\text{int}} \text{ (ps)}^c$	0.40
a_4	0.00
$\tau_{\text{pol}} \text{ (ps)}^d$...
a_3	0.55
$\alpha \text{ (ps}^{-1}\text{)}^e$	5.40
$\omega_0 \text{ (ps}^{-1}\text{)}^f$	6.72





(b) Long-time scan showing the fitted diffusive component (solid line) and the autocorrelation (dash). **(c)** OHD-OKE signal with the diffusive component removed.



(d) Low-frequency spectral distribution for the neat CS_2 . **(e)** Deconvoluted spectral distribution for neat CS_2 and for the three mixtures, corresponding to neat CS_2 (circles), 20% by wt of PS (triangles), 40% by wt of PS (squares), and 60% by wt of PS (stars).