Optical Kerr Effect Measurements on Supercooled Water: the experimental perspective

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Abstract.

The time-resolved spectroscopic investigations are particularly suitable for the measurement of relaxation patterns of complex liquids where several dynamic phenomena, taking place on different time scales, are present. In particular, the optical Kerr effect performed with ultra-short laser pulses and heterodyne detection enables a unique investigation of the dynamic processes taking place in molecular liquids of different natures.

We present here an improved experimental set-up that enables to measure the fast vibrational dynamics and the slow structural relaxation in a single spectrum characterized by low noise and wide dynamic range. We report one measurement of water dynamics in its supercooled phase.

1. Introduction

Time-resolved non-linear spectroscopy, during the last years, showed to be a unique tool for the investigation of dynamic phenomena in complex liquids [1]. In particular, the time-resolved optical Kerr effect (OKE) investigations [2] enable the measurement, in a single high quality data, of the whole dynamics inclusive of the fast vibrational processes and of the slow structural relaxation phenomena. With the implementation of the heterodyne detection (HD-OKE) and thanks to the new reliable laser sources, HD-OKE is becoming a leading technique in the studies of liquids and complex fluids [3].

Several time-resolved HD-OKE studies have been performed on liquid of different natures [3], as for example simple molecular liquids [4] and glass-formers [5, 7, 8]. Also the water dynamics have been investigated by HD-OKE experiments [9, 10, 11, 12, 13] but only one work has been extended to the water supercooled phase [14]. All the HD-OKE investigations of liquid water have shown the presence of a fast vibrational dynamics followed by a slower monotonic relaxation. The initial oscillatory component of the OKE signal provides information about intermolecular hydrogen bond dynamics, whose microscopic origin has still many unclear aspects. The slower decay has been addressed to structural/diffusive relaxation phenomena [14, 15], whose features are particularly evident in the supercooled phase. No detailed HD-OKE investigations of the vibrational dynamics in supercooled water has been carried out, due to the intrinsic experimental difficulties. Indeed the OKE experiment on supercooled water presents two main difficulties:
the very low level of OKE signal produced by liquid water and the intrinsic metastability of the supercooled phase.

Using an improved HD-OKE experimental set-up, we have been able to measure the fast vibrational dynamics and the slow structural relaxation in a single spectrum characterized by low noise and wide dynamic range. Moreover, we succeeded in measuring the dynamics of supercooled water over a large time interval with a high time resolution. We can thus provide an unambiguous measurement of the entire time-dependent correlation function of the water in the supercooled phase.

2. Experimental Set-Up

The time-resolved OKE spectroscopy is a pump-probe technique based on the impulsive generation of a transient birefringence by a laser pulse in an optically isotropic sample. When the pump laser pulse passes through the sample it induces a modification of the optical properties (i.e. a transient optical anisotropy or birefringence). This is a transient effect that relaxes back to the equilibrium state through a variety of processes. A second laser pulse, the probe, is sent through the sample. The transient birefringence, induced by the pump in the sample, modifies the probe polarization state. Since the probe pulse arrives with a controlled time delay, it monitors and measures the transient optical excitation and hence the relaxation processes. Typically, in the time-resolved OKE both the pulses, pump and probe, are polarized and non-resonant with any electronic state.

There are different optical set-up that can be used to perform an OKE experiment [3]. Here we describe our latest experimental set-up based on an improved optical scheme [16] and on an innovative acquisition system [17]. This OKE experiment has shown to be particularly successful to detect low intensity signals in the supercooled water. In the figure 1 we report the optical scheme used. In this scheme, the fast axis of $\lambda/4$ wave-plate is rotated of $\pi/4$ in order to produce a circularly polarized probe field. The two signals, corresponding to the horizontal and vertical linear polarizations generated by polarizer P2, are sent to the balanced photodiode detector. The OKE signal measured in such a way is automatically heterodyned and free from eventual dichroic contributions [16]. A further improvement of the OKE signal is obtained subtracting the two HD-OKE measurements, corresponding at left and right circular polarizations of the probe field (i.e. $\pm \pi/4$ positions of the wave-plate axis). This procedure removes from the signal the spurious dichroic contributions coming from possible misalignment of the wave-plate (i.e. angle of rotation different from $\pi/4$). Here we are using a real-time acquisition of the experimental signal during the rapid scan of the optical delay line [17]. This acquisition scheme enables data acquisition with high absolute time resolution, $\approx 1$ fs, high scanning velocity, $\leq 2.5$ [cm·s$^{-1}$], and long time delay, few ns. In figure 2 we report the complete experimental scheme. The laser is a high repetition-rate Kerr-lens mode-locked Ti:sapphire laser (FemtoRose 10MDC, by R&D Ultrafast Laser) pumped by the second harmonic of a laser-diode-pumped Nd:YVO$_4$ laser.

![Figure 1](image-url)
3. HD-OKE signal on supercooled water

The signal beam measured in an HD-OKE experiment is [3, 5, 7]:

\[ S_{hd}(\tau) \propto \int dt \left| E_{pr}(t - \tau) \right|^2 \int dt' R_{oke}(t - t') \left| E_{ex}(t') \right|^2 \]  

being \( E_{pr} \) and \( E_{ex} \) the probing and exciting laser pulses, respectively; \( R_{oke}(t) \) is the material response function. Since we are performing a non-resonant OKE experiment, the Born-Oppenheimer approximation applies and the response function becomes [3]:

\[ R_{oke}(q, t) \propto -\frac{\theta(t)}{k_B T} \frac{\partial}{\partial t} \langle \chi_{ij}(t) \chi_{ij}(0) \rangle \]  

Where \( \chi_{ij} \) is linear susceptibility, \( \langle \cdot \rangle \) is the ensemble average, \( T \) is the temperature, \( k_B \) is the Boltzmann constant and \( \theta(t) \) the Heaviside step function. \( \mathcal{R}(t) \) defines all the material dynamic information.

In figure 3 we report, as example, a HD-OKE signal obtained in a supercooled water sample at a temperature of \( T = -24 \, ^\circ C \). This HD-OKE experiment enables the measurement of the fast vibrational dynamics and the slow structural relaxation in a single data, from about 20 fs to 35 ps. This data confirms the presence of a non-exponential monotonic decay, from about 1 ps to 35 ps, that has to be addressed to the slow structural/diffusive relaxation [14]. In the fast time scale, up to about 1 ps, the HD-OKE signal displays a complex oscillatory pattern. This signal features are due to the inter-molecular vibrational dynamics of the hydrogen bound structure.

(Millennia V, by Spectra-Physics) with a pulse width of 20 fs [17].
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