

# Precise and Rapid Detection of Optical Activity for Accumulative Femtosecond Spectroscopy

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**Abstract.** We present a fast and sensitive polarimeter combining common-path optical heterodyne interferometry and accumulative spectroscopy to detect rotatory power. The sensitivity of rotatory detection is determined to be 0.10 milli-degrees for a measurement time of only one second and an interaction length of 250  $\mu\text{m}$ . Its suitability for femtosecond studies is demonstrated in a non-resonant two-photon photodissociation experiment.

## 1 Introduction

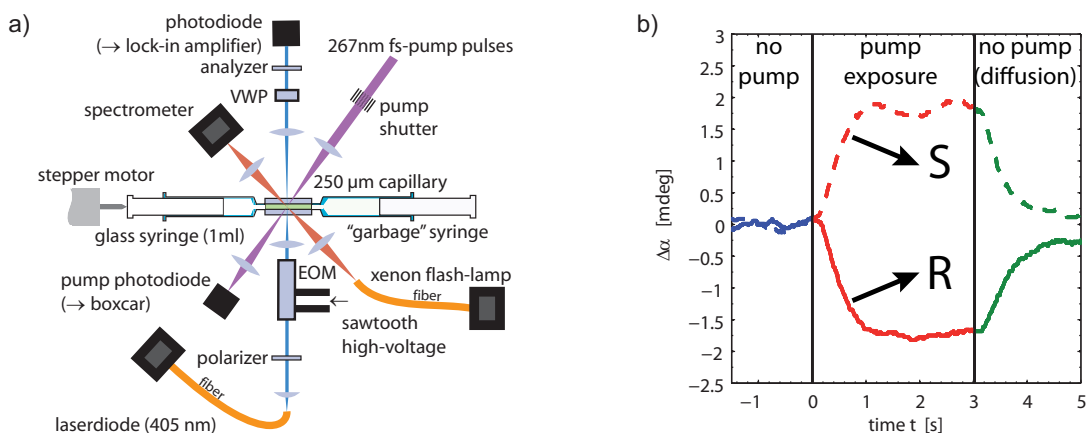
Measuring the optical activity is a common spectroscopic technique to identify excesses of chiral molecules. Large optical path lengths, long integration times and high concentrations are typically employed to reach measurable optical rotation angles. Such conditions can hardly be met in femtosecond (fs) spectroscopy, hence optical rotation has been used only recently as a probing signal in liquid-phase ultrafast studies [1–5]. We have developed a polarimeter to overcome these intricacies. Albeit it does not probe ultrafast chirality changes, it is suitable for probing ultrafast dynamics initiated with fs laser pulses by monitoring optical rotation changes due to the emergence of a stable photoproduct.

## 2 Experimental setup

We modify the heterodyne detection method of Lee and Su [6] and combine it with the recently developed accumulative technique that further enhances sensitivity [7, 8]. To demonstrate the device's capabilities, we employ chiral methyl p-tolyl sulfoxide which undergoes a bond cleavage at the stereogenic center after UV irradiation [9], leading to non-chiral fragments. The polarimeter setup is sketched in Fig. 1a. The light of a continuous-wave (CW) laser diode passes a fixed polarizer before the polarization is continuously modulated by an electro-optic modulator (EOM). Then, the light is focused weakly into the optically active sample in the capillary. Subsequently, a variable wave plate (VWP) of Berek-type, with its optical axis parallel to the polarizer, is passed before the light reaches the analyzer oriented at  $45^\circ$  relative to the polarizer. The detected signal can be calculated via the Jones formalism leading to a sinusoidal signal as a function of the EOM voltage, whose amplitude and phase is determined by a lock-in amplifier. The phase of the signal only depends on the (known) retardation setting of the VWP and the optical rotation  $\alpha$  of the sample, enabling us to calculate the optical rotation change  $\Delta\alpha$  directly [10]. Besides the detection of  $\Delta\alpha$ , the linear absorption (beam which is detected by the spectrometer in Fig. 1a) is recorded simultaneously by utilizing weak xenon flash-lamp pulses.

Furthermore, to initiate the photoreaction, a beam with fs laser pulses at  $\lambda = 267$  nm is spatially overlapped with the other beams in the capillary and can be blocked by a mechanical pump shutter. In the accumulative spectroscopy scheme the same sample volume is irradiated with several subsequent pump pulses while the measurement proceeds, and then the complete sample volume is exchanged by moving a stepper motor pushing the plunger of the glass syringe holding the sample [7, 8].

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**Fig. 1.** a) Three beams are spatially overlapped in the capillary to record the linear absorption (detection by spectrometer) as well as the optical rotation (detected by photodiode) before, during and after illumination with fs laser pulses. b) Optical rotation change  $\Delta\alpha$  for both the R- (solid) and S-enantiomer (dashed) of methyl p-tolyl sulfoxide (averaged over 10 measurements). Before pump illumination ( $t < 0$  s) a constant signal is acquired, corresponding to zero optical rotation change. During the pump exposure ( $0 < t < 3$  s) the optical rotation changes due to the photodecomposition of the chiral reactants, giving rise to a negative (R) or positive (S) signal. After the end of illumination ( $t > 3$  s) the optical rotation change vanishes again due to diffusion effects.

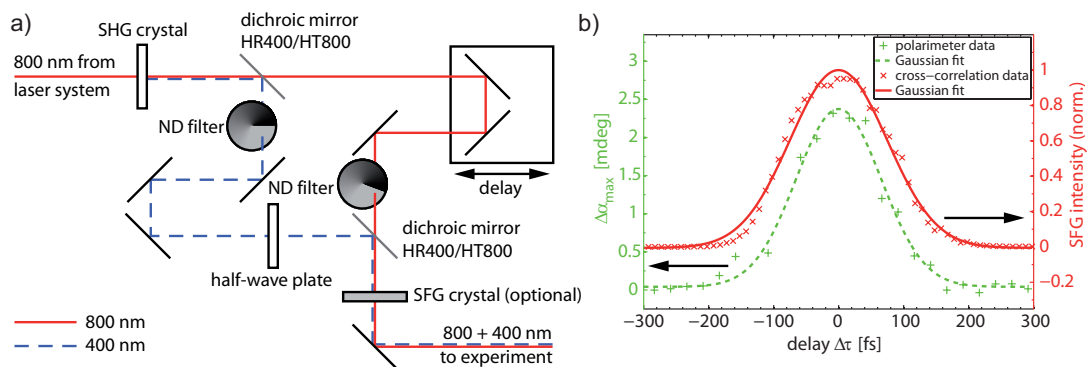
### 3 Data acquisition and optical rotation resolution

At the start of a measurement the stepper motor is moved to renew the sample solution in the capillary. Afterwards the data acquisition of the polarimeter probe and the linear absorption probe begins. The pump shutter is opened after 1.5 s to start the photoreaction of the chiral molecules. After three seconds of illumination the pump shutter is closed again, but the measurement is continued for another two seconds. Then, the sample volume is exchanged via the stepper motor and the measurement cycle starts all over. Since we are only interested in optical rotation changes  $\Delta\alpha$  the first 1.5 seconds (see Fig. 1b) are used to acquire a reference point with no optical rotation change. During illumination ( $0 < t < 3$  s) the photoreaction proceeds and  $\Delta\alpha$  de- or increases, depending on which enantiomer is present in the capillary. After the pump illumination ( $t > 3$  s) the optical rotation vanishes again due to diffusion. Hence, Fig. 1b shows enantiodifferentiating signals at high signal-to-noise ratio, indicating that the photodestruction can be monitored successfully, which is furthermore corroborated by the simultaneously acquired linear absorption signal (data not shown, see Ref. [10]).

By comparing to the noise level of the optical rotation while the capillary is only filled with solvent, we can determine the resolution of the polarimeter experimentally to 0.10 milli-degrees (mdeg) at an optical path length of 250  $\mu\text{m}$  with only one second of measurement time. Compared to commercially available devices with interaction lengths of centimeters and measurement times of roughly 10 s, our setup exhibits higher speed and sensitivity for optical rotation detection, but even in a geometry suitable for fs spectroscopy.

### 4 Femtosecond time resolution

To gain fs time resolution, a pair of pump pulses, delayed with respect to each other (Fig. 2a), is employed. In the displayed example the photoreaction is initiated via a non-resonant absorption of two photons of different color. The optical rotation signal as a function of the relative time delay  $\Delta\tau$  reflects the time resolution of the setup and should follow the cross-correlation of the pump pulse pair if a true non-resonant two-photon transition is excited. The pulse pairs are generated by partly frequency doubling the 800 nm output of the fs laser system in a second-harmonic generator (SHG) process and subsequent separation of 800 nm and 400 nm beams in a Mach-Zehnder-type setup (Fig. 2a). The



**Fig. 2.** a) Sketch of the setup used to introduce the time delay between the two pump pulses. The half-wave plate is included to achieve parallel polarizations. For the cross-correlation measurement, an SFG crystal is included after the second dichroic mirror. b) Comparison of the cross-correlation and the polarimeter measurement with two pump pulses. The shapes of both curves are nearly identical, as can be seen from the two Gaussian fits. The data sets are vertically offset for clarity, arrows indicate the corresponding ordinates.

two beams are individually attenuated in such a way that the photoreaction is not observed if only one beam is used. For every value of  $\Delta\tau$ , a measurement curve analogous to Fig. 1b is recorded. The maximum optical rotation change  $\Delta\alpha_{\max}$  is then plotted as a function of  $\Delta\tau$ .

The result for a measurement with the S-enantiomer is presented in Fig. 2b (plus signs, Gaussian fit as dashed line) and is juxtaposed with a cross-correlation via sum-frequency generation (SFG) of the two pump pulses (crosses, Gaussian fit as solid line). Comparison of the curves discloses their identical temporal behavior. Hence, the time resolution of the accumulative polarimeter setup is indeed predominantly limited by the pulse duration of the fs laser system. Note that no ultrafast change in optical rotation is detected, but a change in optical rotation between reactants and stable products is probed by a CW light source.

## 5 Summary

In summary, we presented a sensitive polarimeter setup combining common-path optical heterodyne interferometry and accumulative femtosecond spectroscopy to measure small changes in optical rotation. Ultrafast time resolution is obtained by utilizing a pair of pump pulses, so that chemical photoreaction dynamics may be revealed if a stable photoproduct with a different optical activity than the reactant is formed after the interaction with two femtosecond laser pulses with proper temporal delay.

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