

Discriminating Racemic from Achiral Solutions with Femtosecond Accumulative Spectroscopy

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Abstract: We follow asymmetric photodissociation reactions of chiral substances with a sensitive polarimeter specifically designed for applications with femtosecond pulses. The accumulative detection scheme allows the discrimination of racemic and achiral solutions with high sensitivity.

OCIS codes: (120.5410) Polarimetry; (300.6310) Spectroscopy; (350.3450) Laser-induced chemistry

1. Introduction

Steady-state circular dichroism (CD) or optical activity are common techniques to analyze chiral samples. However, the utilized long optical path lengths, high concentrations, and long integration times are not suitable for ultrafast spectroscopy. Some of those challenges could be overcome by various techniques [1], which however cannot discriminate a racemic sample from an achiral one. A recent gas-phase technique employing femtosecond (fs) laser pulses has the potential to do so [2]; here we want to explore this issue in the liquid phase with a different approach.

2. Measurement Principle

In order to be able to discriminate between racemic and achiral solutions by optical means one has to generate a chirality-sensitive signal. We chose to generate an enantiomeric excess (ee) [3] with circularly polarized fs pulses. Since the difference of the absorption coefficients for left- or right-circularly polarized light is very small, we employ an accumulative measurement scheme with our sensitive polarimeter [4]. In our scheme, not only one pump pulse is used, but several subsequent fs laser pulses irradiate the same sample volume and initiate the photoreaction.

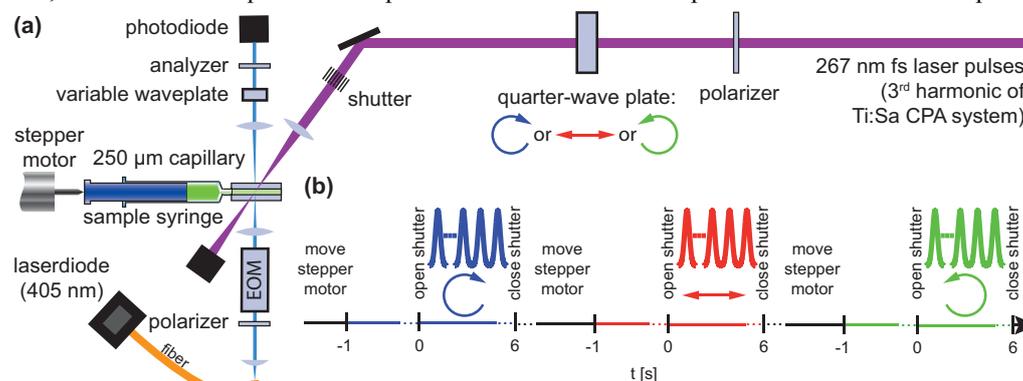


Fig. 1. (a) Pump (purple) and probe (blue) beams are spatially overlapped in the 250 μm capillary to record the optical rotation before and during illumination with fs laser pulses. The polarization state (lpl, lcpl, rcpl) of the pump beam is controlled via a linear polarizer and a quarter-wave plate. (b) The measurement cycle consists of three single accumulation steps with rcpl, lpl, and lcpl. Before the recording of the optical rotation starts, fresh sample is pushed into the capillary in every case. After one second of recording the shutter is opened for 6 s.

The setup and measurement scheme is depicted in Fig. 1a. We employ a sensitive polarimeter to detect the optical rotation (OR) change $\Delta\alpha$ in the capillary with only 250 μm optical path length [4]. The polarization of the 267 nm pump pulses is varied between left- (lcpl) and right-circularly (rcpl), as well as linearly polarized (lpl) light. For each polarization the following measurement procedure is conducted: the sample in the capillary is renewed and the acquisition of $\Delta\alpha$ is started; after 1 s (needed to record a reference value for $\Delta\alpha$ [4]), the pump shutter is opened at $t = 0$ and the sample is irradiated with UV laser pulses for 6 s, while $\Delta\alpha$ is continuously recorded (see Fig. 1b).

3. Results

We utilize polarized UV fs laser pulses at 267 nm to trigger an asymmetric photoreaction of the racemic mixture of 1,1'-binaphthyl-2,2'-diyl hydrogenphosphate, leading to achiral photoproducts. In Fig. 2a, the CD spectra of the pure enantiomers and the racemate dissolved in methanol ($c = 13.5$ mg/ml) are depicted. Obviously, the CD signal does not reveal whether an unknown solution is racemic or contains achiral molecules. Whereas the pump pulse excites

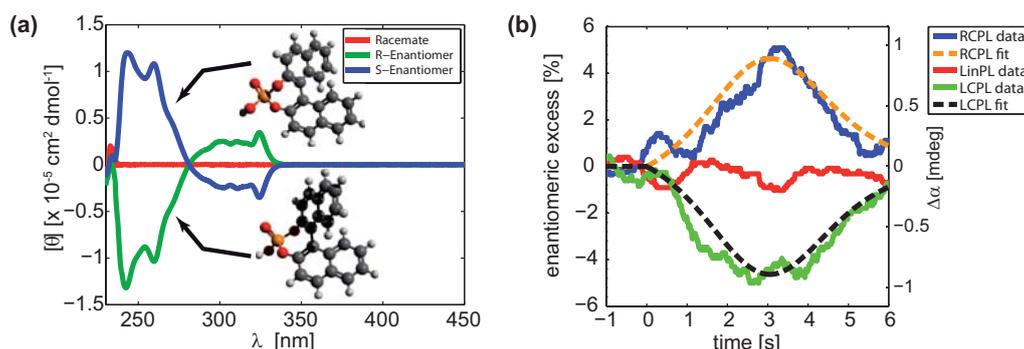


Fig. 2. (a) Steady-state CD spectra of racemic binaphthol (red) and for the pure enantiomers (green, blue). The Cotton effect for the electronic transition centered at 280 nm is clearly visible. (b) Experimental outcome of an accumulative OR experiment with racemic solution. While lpl (red) does not change the ee, circularly polarized light leads to an enrichment of one or the other enantiomer. The dashed lines correspond to the fitting model.

the molecules, our probe wavelength of 405 nm is in a spectral region where they do not absorb at all.

The result of an OR measurement using the scheme of Fig. 1 with racemic solution is shown in Fig. 2b. In the case of lpl pump pulses, no change in OR is visible (right axis). In contrast, rcpl fs pulses (blue) lead to a positive change, while for lcpl pulses (green) the sign flips. For both circular polarizations a clear extremum is visible. This behavior can be explained as follows. With UV pump pulses these molecules undergo a bond cleavage to form non-chiral fragments. Depending on the handedness of the polarization, more R- or S-enantiomers are gradually converted, leading to the generation of ee. Due to the small difference of the absorption coefficients of both enantiomers for lrcl or rcpl, one fs laser pulse would not lead to a detectable signal. However, since we accumulate the outcome of several subsequent photoreactions, this photo induced ee can be magnified and hence observed.

We model the data by solving the differential equation for the time-dependent change in the number of molecules N_{Mol} after irradiation with a given number of photons N_{ph} for lcpl or rcpl. By subtracting the solution for lcpl with the corresponding absorption cross section σ_l from the solution for rcpl (σ_r) one arrives at

$$N_{Mol}(t) = \sigma_r \log_{10} \left(10^{-\sigma_r N_0} + 10^{-\sigma_r N_{ph} t} - 1 \right) - \sigma_l \log_{10} \left(10^{-\sigma_l N_0} + 10^{-\sigma_l N_{ph} t} - 1 \right) \quad (1)$$

where N_0 corresponds to $N_{Mol}(t=0)$. Equation (1) is symmetric if one exchanges σ_l with σ_r . Hence, the two curves for the circular polarizations must also be mirror images since the OR scales with the number of chiral molecules present in the solution. Fitting both curves together (orange and black dashed lines in Fig. 2b) the resulting parameters reveal that the absorption cross sections for lcpl and rcpl differ by only 0.0085%.

In order to further quantify the induced ee, we perform experiments with just one enantiomer (not shown) and determine the maximal possible $\Delta\alpha$ (in analogy to [4]), which is 19.18 mdeg. Assuming the ee scales linearly with the OR, we calculate the relative ee value (left axis of Fig. 2b), revealing an ee of several percent.

4. Discussion and Outlook

For an exemplary racemic solution, we monitored the evolution of photo induced ee, which reaches several percent at a certain illumination time and decreases again for continued exposure to UV light. This is a direct demonstration that the approach allows the discrimination of racemic and achiral solutions if the pump pulses generate stable achiral photoproducts. Furthermore, if the pump illumination is stopped at the right moment, this ee persists in the sample volume and might be exploited for other purposes. Among those, quantum control approaches could be beneficial, since the setup allows for fs time resolution [4] if pump pulse pairs or possibly shaped fs laser pulses are employed. Future experiments could further investigate the ultrafast dynamics of chiral molecules from which achiral products are formed in a stepwise manner, necessitating several interactions with fs pump pulses.

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