A broadband femtosecond time-resolved circular dichroism spectrometer in the near-UV

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A femtosecond time-resolved circular dichroism setup operating at 20 kHz in the near-UV spectral range is presented. The spectrometer employs broadband probe (260 – 360 nm) and tunable narrowband pump pulses (1.5 nm FWHM) over the same spectral range.

Time-resolved electronic circular dichroism spectroscopy (TRCD) is a promising experimental technique that is sensitive to changes in biomolecular configuration on ultrafast timescales [1]. It offers a unique opportunity to combine the time-dependent electronic information provided by traditional transient absorption spectroscopy with the structural information encoded in the chirality of molecular systems. Nevertheless, technical challenges have only allowed for slow progress with regards to the experimental implementation of TRCD [2].

Here we present an experimental scheme that overcomes these issues by employing broadband femtosecond probe pulses (260 – 360 nm, 100 fs) at a high repetition rate (20 kHz) and low intensity noise (< 1% rms) with a shot-to-shot data acquisition system [3]. The scheme is based on the self-heterodyne detection technique employed by Helbing and co-workers for vibrational TRCD, where the ellipticity of the probe pulse is switched between left- and right-handed by a photoelastic modulator [4]. Additionally, a high quality polarizing beamsplitter is used to separate and simultaneously acquire the sample's transient circular dichroism and absorption spectra. The capabilities of the setup are evaluated via its application to enantiomerically pure samples of Δ,Λ-$[Ru(bipy)_3]^{2+}$.

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