Control and Spectroscopy of Chiral Systems in the Condensed Phase

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Moshe Shapiro has been a pioneer in suggesting schemes for coherent control of chiral systems. In this presentation, progress will be shown toward experimental realizations of chirally selective control and time-resolved chiral spectroscopy of molecules in the condensed phase. For this purpose, a variety of fundamental or practical issues have to be addressed. Solutions to some of the problems will be presented.

As a means to introduce chirality via light in the most flexible fashion, we have developed vector-field shaping with independent ultrafast control over amplitude, phase, and polarization of an ultrashort pulse or pulse sequences, as a function of time [1].

Another ingredient for chiral control is a detection method that provides chiral sensitivity. As one possibility, we have constructed a highly sensitive polarimeter, together with accumulative spectroscopy, to measure the optical rotation change upon a chirality-modifying photochemical reaction [2]. A second option is to measure a photoinduced change in circular dichroism (CD). Femtosecond time-resolved CD spectroscopy is challenging and prone to artefacts, thus in the literature single-wavelength detection is generally employed. We have developed broadband time-resolved CD spectroscopy [3]. It is based on a setup that can create a copy, as well as its precise polarization-mirrored image, of any (polarization-shaped) input laser pulse. Thus we can switch between opposite chiralities of the (probing) laser field on a shot-to-shot basis and measure broadband time-resolved CD spectra via recording their difference.

Data acquisition times are often long owing to low signal strength. We have used a high-repetition-rate (100 kHz) laser and implemented shot-to-shot transient absorption spectroscopy where complete probe spectra are recorded for each laser shot and the pump pulses are chopped synchronously at 50 kHz [4]. This dramatically decreases measurement time, by a factor of up to 100, as compared to 1 kHz integrated readout.

When performing time-resolved spectroscopy or control of population dynamics (such as of chemical reactions) one has to take care that anisotropic contributions to the signal are avoided. With linearly polarized pump and probe pulses in transient absorption spectroscopy, the "magic angle" configuration is commonly employed. However, for pulses with other polarizations the situation is more complicated. We have derived a condition for anisotropy-free measurements with arbitrary polarizations [5].

Assembling several of the above "ingredients," we demonstrate all-optical discrimination between racemic and achiral molecular solutions. This is possible despite the fact that both samples are neither optically active nor exhibit a CD effect [6]. In a second experiment, we probe molecular structural rearrangement via time-resolved CD spectroscopy [3].

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