TWO-DIMENSIONAL SUBPICOSECOND TIME-RESOLVED FLUORESCENCE ANISOTROPY: OPTICAL KERR-GATING WITH A DYNAMIC POLARIZATION EXCITATION.

TAKASHIGE FUJIWARA, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus OH 43210*; NATALIE C. ROMANO, DAVID A. MODARELLI, and EDWARD C. LIM, *Department of Chemistry and The Center for Laser and Optical Spectroscopy, The University of Akron, Akron OH 44325-3601*.

With an advent of ultrafast lasers, a number of applications are widely adopted to probe photophysical and photochemical properties of a molecule that occurs in an ultrafast (femtosecond to picosecond) time scale. Intramolecular charge transfer (ICT) or proton transfer in photoexcited electron donor–acceptor (EDA) molecules, for instance, has been a topic of very extensive time-resolved studies for several decades. Time-evolution of an anisotropic property can track dipole orientations or conformational changes in their photoexcited molecular systems, which is of extreme importance to examine its structure and excited-state dynamics rather than probing an isotropic population change.

With this respect, we recently developed a subpicosecond time-resolved 2-D fluorescence anisotropy (TRFA) in which method implements a dynamic alternation of laser polarizations to excite a sample using a photoelastic modulator (PEM). In the combination of an ultrafast optical shutter (Kerr-gating) and a spectrograph that is coupled with a CCD, two signal phases so-obtained dynamically, $I_{\parallel}(t,\lambda)$ and $I_{\perp}(t,\lambda)$, provide a 2-D mapped information on both a wide range for spectra and time-resolved kinetics of photoexcited molecules of interest. From the definition of an anisotropy 2-D TRFA, $r(t,\lambda)$, is given instantly and even more reliably at a single measurement. In this paper we will present benchmark tests of some target samples to establish performance of TRFA.