

TIME-RESOLVED SIGNATURES ACROSS THE INTRAMOLECULAR RESPONSE IN SUBSTITUTED CYANINE DYES

MUATH NAIRAT, MORGAN WEBB, MICHAEL ESCH, VADIM V. LOZOVY, BENJAMIN G LEVINE,
MARCOS DANTUS, *Department of Chemistry, Michigan State University, East Lansing, MI, USA.*

The optically populated excited state wave packet propagates along multidimensional intramolecular coordinates soon after photoexcitation. This action occurs alongside an intermolecular response from the surrounding solvent. Disentangling the multidimensional convoluted signal enables the possibility to separate and understand the initial intramolecular relaxation pathways over the excited state potential energy surface. Here we track the initial excited state dynamics by measuring the fluorescence yield from the first excited state as a function of time delay between two color femtosecond pulses for several cyanine dyes, having different electronic configurations. We find that when the high frequency pulse precedes the low frequency one and for timescales up to 200 fs, the excited state can be depleted through stimulated emission with efficiency that is dependent on the molecular electronic structure. A similar observation at even shorter times was made by scanning the chirp (frequencies ordering) of a femtosecond pulse. These changes reflect the rate at which the nuclear coordinates of the excited state leave the Franck-Condon (FC) region and progress towards achieving equilibrium. Through functional group substitution, we explore these dynamic changes as a function of dipolar change following photoexcitation. We show that with proper knowledge and control over the phase of the excitation pulses, we can extract the relative energy relaxation rates through which the early intramolecular modes are populated at the FC geometry soon after excitation