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Title: Early Time Solvation Dynamics Probed by Spectrally Resolved Degenerate Pump-Probe

Spectroscopy

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Abstract:

The dynamic role of solvent in influencing the rates of physico-chemical processes (for example, polar solvation and electron transfer) has been extensively studied using time-resolved fluorescence spectroscopy. Here we study ultrafast excited state relaxation dynamics of three different fluorescent probes (DNTTCI, IR-140 and IR-144) in two polar solvents, ethanol and ethylene glycol, using spectrally resolved degenerate pump-probe spectroscopy. We discuss how time-resolved emission spectra can be directly used for constructing relaxation correlation function, obviating spectral reconstruction and estimation of time-zero spectrum in non-polar solvents. We show that depending on the specific probe used, the relaxation dynamics is governed either by intramolecular vibrational relaxation (for IR140) or by intermolecular solvation (for DNTTCI) or by both (for IR144). We further show (using DNTTCI as a probe) that major differences in solvation by ethanol and ethylene glycol is contributed by early time (<1 ps) dynamics.

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