Signal Enhancement in Pump-Repump-Probe Spectroscopy Using a Sequential Pulse Train

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Pump-repump-probe spectroscopy using two excitation pulses is a powerful tool for investigating reaction dynamics in higher excited states (S_n states). The pump pulse excites the ground state molecule into the intermediate state, which is further pumped up to the higher excited state by the repump pulse, and the resultant dynamics therein is monitored by the probe pulse. The transient signals, however, are rather weak (typically ~10^{-3} OD) and often difficult to detect due to the limited portion of molecules populated into the higher excited state upon the two sequential excitations. In the present study, we have developed a method for enhancing the transient signal using a sequential pulse train and demonstrated its application to photoionization dynamics of perylene in solution. Figure 1a shows schematic diagram of signal enhancement in pump-repump-probe spectroscopy. We generated a collinear 32-pulse train with 5 birefringent crystals and used it as the pump beam, thereby enabling us to increase the excitation portion of the intermediate without undesirable nonlinear optical effects. Figure 1b shows transient absorption spectra of perylene in acetonitrile excited with a pulse train at 400 nm (pump) and a subsequent pulse at 700 nm (repump). The delay time is defined as an interval between the repump and probe pulses, and ΔΔAbsorbance is differential absorbance between in the presence and absence of the repump pulse. At the time zero, negative and positive bands, which are respectively ascribable to the S_1 bleaching and absorption from the S_n state, are observed at 690 and 500 nm with signal intensity of -0.15 and +0.03 OD. This result clearly shows that the transient signals are amplified by a factor of a few tens under the present excitation condition.

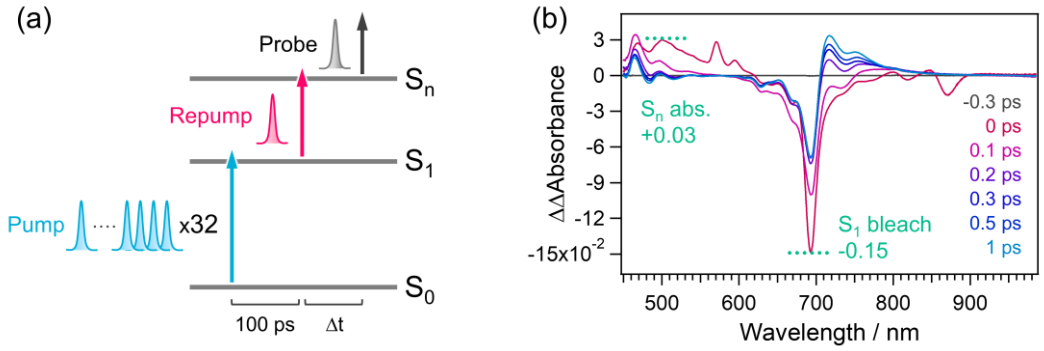

Figure 1. (a) Photoexcitation scheme with a sequential pulse train. (b) Transient absorption spectra of perylene in acetonitrile excited with the pump (400 nm, 3 μJ) and repump (700 nm, 300 nJ) pulses.