Supporting Information

Development of Vibrational Frequency Maps for Nucleobases

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Measurement of the vibrational lifetime of the GMP carbonyl stretch

Experimental determination of the vibrational lifetime of the nucleobase carbonyl stretching mode was conducted by Dr. Paul Sanstead and Professor Andrei Tokmakoff. The vibrational lifetime of the 1665 cm^{-1} peak of the guanosine 5'-monophosphate (GMP) carbonyl stretching mode was measured through a waiting time (τ_2) series of 2D IR spectra, using the methods described in Reference 1. GMP was purchased from Sigma-Aldrich and used without further purification. Labile protons were H-D exchanged in heavy water (D_2O, Cambridge Isotopes, D 99.9%) and the nucleotides were lyophilized prior to use. Samples were prepared at 3 mg/mL concentration in D_2O. Spectra were measured at room temperature. The coherence time was stepped from -160 to 2500 fs in 4 fs steps. The waiting times sampled were 150, 250, 350, 500, 750, 1000, 1500, 3000, and 5000 fs. Surfaces were collected with both parallel (ZZZZ) and perpendicular (ZZYY) polarizations, and then added together $S_{zzzz} + 2S_{ZZYY}$ to produce isotropic surfaces that are independent of orientational dynamics in τ_2. Figure S1 shows the 2D IR spectrum measured at each waiting time. To characterize the vibrational lifetime of the 1665 cm^{-1} GMP carbonyl stretch, the integrated ground state bleach of this mode was tracked across the series of waiting times. The lower right panel in Figure S1 shows the normalized integrated intensity as a function of waiting time. The amplitude trend was fit to a single exponential decay, resulting in a time constant of T_1 = 649 fs.

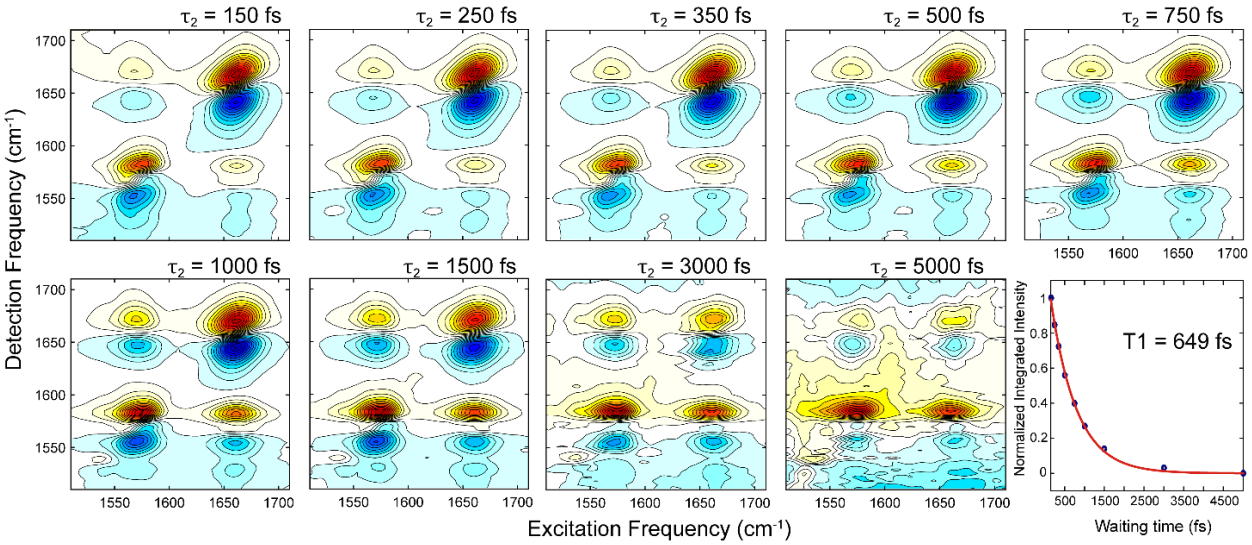

Figure S1. The room temperature 2D IR spectrum of 3 mg/mL GMP in D_2O measured at τ_2 = 150, 250, 350, 500, 750, 1000, 1500, 3000, and 5000 fs. The vibrational lifetime of the 1665 cm^{-1} GMP carbonyl mode was measured by tracking the decay of the intensity of the ground state bleach. The lower right panel shows a fit of this decay to a single exponential in which T_1 = 649 fs.

References

1. Sanstead, P. J.; Stevenson, P.; Tokmakoff, A., Sequence-Dependent Mechanism of DNA Oligonucleotide Dehybridization Resolved through Infrared Spectroscopy. *J. Am. Chem. Soc.* **2016,** *138* (36), 11792-11801.