Supplementary Information:

FTIR:

All FTIR absorption spectra were acquired with a Thermo Nicolet 6700 spectrometer. The peak extinction coefficient was determined from the dependence of the optical density on the concentration maintaining the same sample cell pathlength.

2D IR Method:

The phase-matched signal was detected by heterodyning with a local oscillator pulse that preceded it by a fixed interval of ~1.5 ps. The time interval between pulse 1 and 2 is denoted as τ, the coherence time, and the time between pulses 2 and 3 is denoted as T, the waiting time. The rephasing and nonrephasing signals arise when the k_1 pulse arrives earlier or later than k_2. The signal and local oscillator pulses are combined at the focal plane of a monochromator equipped with a 64 element mercury-cadmium-telluride array detector (InfraRed Associates, Stuart, FL). Each detector element is 200 μm in width and 1 mm in height. The monochromator has a focal length of 190 mm with a 100 lines per mm groove grating was used in our experiments. All 2D IR spectra were obtained by sampling a coherence time from -5 to 5 ps in steps of 2 fs.

Linear FTIR fitting:

The magnitudes of T_2^*, Δ_1^2, and Δ_2^2 are recovered from fitting the experimental linear IR lineshapes using the following equation,

$$(1) \qquad I(\omega) = 2\,\mathrm{Re}\int_0^\infty \exp\left(i\left(\omega - \langle\omega_{10}\rangle\right)t\right) \times \exp\left(-g(t) - t/2T_{10} - 2Dt\right)dt,$$

where $g(t) = \int_0^t d\tau_1 \int_0^{\tau_1} \langle \delta\omega_{10}(\tau_2)\,\delta\omega_{10}(0)\rangle\, d\tau_2$, T_{10} is the population relaxation time, and D is the rotational diffusion coefficient. The relaxation time, T_{10}, was determined from the signal decay of the diagonal peaks as a function of waiting time. A rotational diffusion coefficient of 50 ps was assumed based on fluorescence anisotropy decays found in literature.[1] The T_2^* and Δ_1 are required that best fit both the linear spectrum and the 2D IR spectra. In general, it has been shown that calculations of the linear spectrum result in

several pairs of parameters that reproduce the appropriate bandwidth for a given value of τ_1 while fitting the linear spectrum reasonably well.[2]

A simulation of the 2D IR spectra was carried out including all relevant Liouville pathways[3] using the model FFCF described in main text. Diagrams representing ground-state bleaching $\{0i|00|i0\}$, stimulated emission $\{0i|ii|i0\}$, and excited-state absorption $\{0i|ii|i+i,i\}$ were included along with their nonrephasing counterparts, where i is the V=0 $\rightarrow$ V=1 region state and $i+i$ is the eigenstate involved in V=1 $\rightarrow$ V=2 region transitions of the N_3 stretch. The inhomogeneous and homogeneous parameters were incorporated through the use of the FFCF. The 2DIR spectra are simulated for 150 fs and 1.5 fs, where the correlation is the greatest and where the frequency correlation has almost completely decayed, respectively. The change in the slope and the spectral shape changes from tilted at an angle of 30 degrees from the ω_τ axis to an angle 13^o for both experiment and simulation. It is clear that this model provides both a reasonable fit to the FTIR spectrum and still captures the 2D IR spectral shapes.

1 D. Onidas, D. Markovitsi, S. Marguet, A. Sharonov and T. Gustavsson, *J. Phys. Chem. B*, 2002, **106**, 11367-11374.
2 D. G. Kuroda, D. Y. Vorobyev and R. M. Hochstrasser, *J. Chem. Phys.*, 2010, **132**.
3 N. H. Ge, M. T. Zanni and R. M. Hochstrasser, *J. Phys. Chem. A*, 2002, **106**, 962-972.