Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supporting Information

Ultrafast IR Spectroscopy of Polymeric Cytosine Nucleic Acids Reveal the Long-lived Species is due to a Localised State

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Biexponential Fits

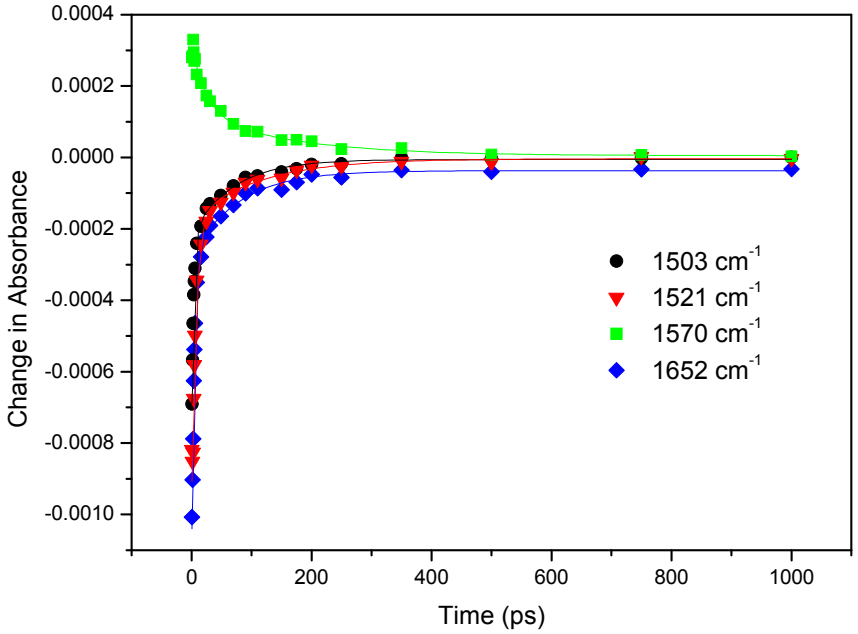

Figure S1. Biexponential fits for 10 mM dC_{30} in 50 mM Na_2HPO_4 (pH 8.5, single stranded) in D_2O at 1503, 1521, 1570 and 1652 cm^{-1}. Delays (ps): 1, 2, 3, 4, 5, 6, 9, 11, 25, 31, 49, 70, 90, 110, 150, 175, 200, 250, 350, 500, 750 and 1000.

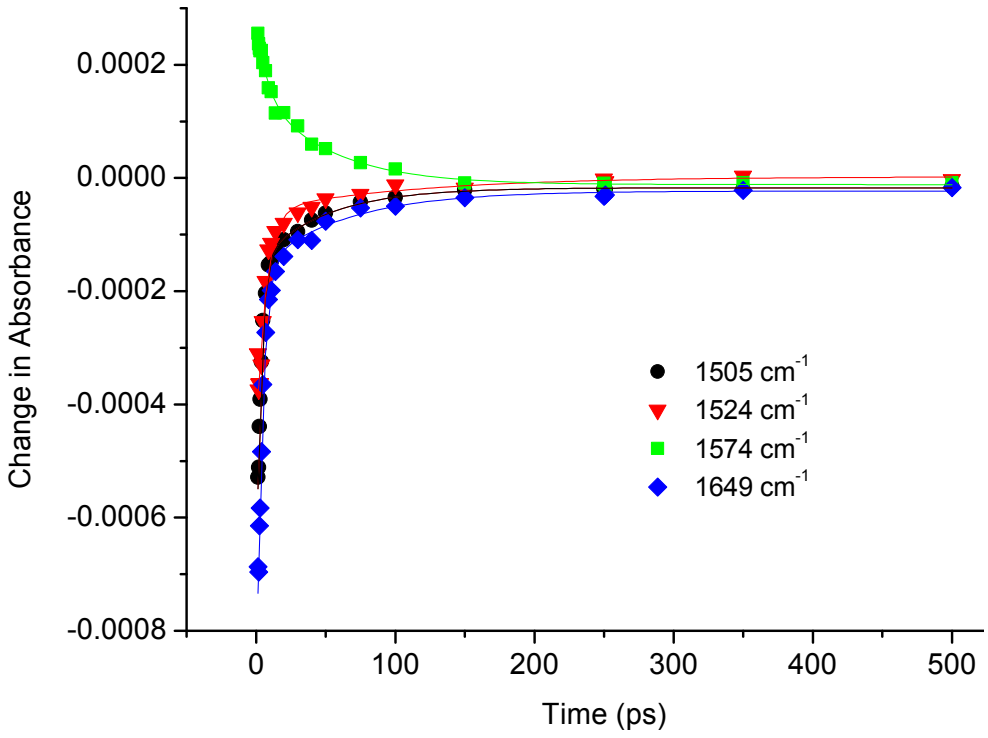

Figure S2. Biexponential fits for 10 mM rCMP in 50 mM phosphate D_2O buffer (pH 7) at 1505, 1524, 1575 and 1649 cm^{-1}. Delays (ps): 2, 2.5 3, 4, 5, 7, 9, 11, 14, 20, 30, 40, 50, 75, 100, 150, 250, 350 and 500.

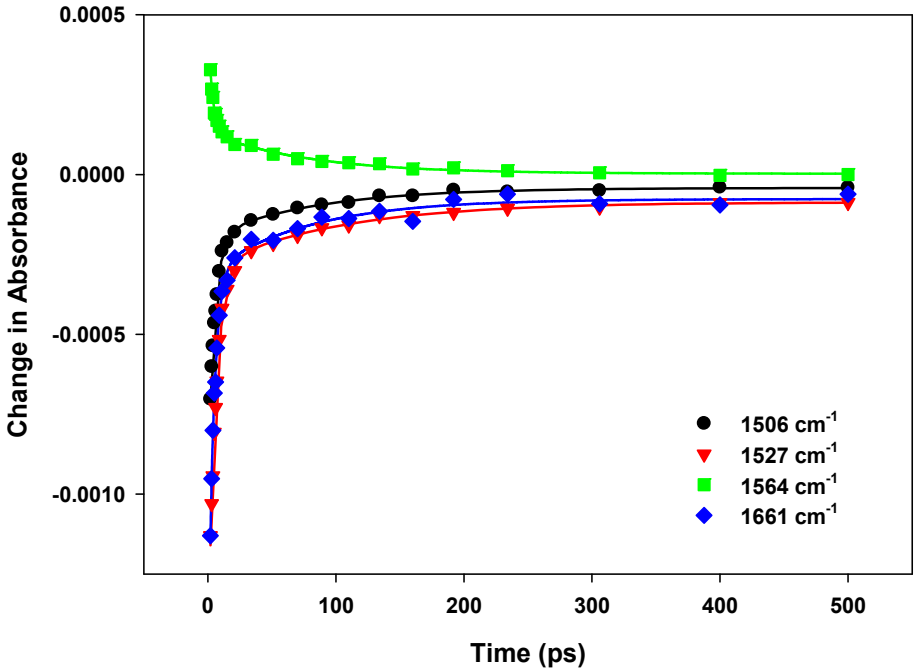

Figure S3. Biexponential fits for 10 mM poly(rC) in 50 mM phosphate D_2O buffer (pH 7) at 1506, 1527, 1564 and 1661 cm^{-1}. Delays (ps): 2, 3, 4, 5, 6, 7, 9, 11, 15, 21, 34, 51, 70, 89, 110, 134, 160, 192, 234, 306, 400 and 500.

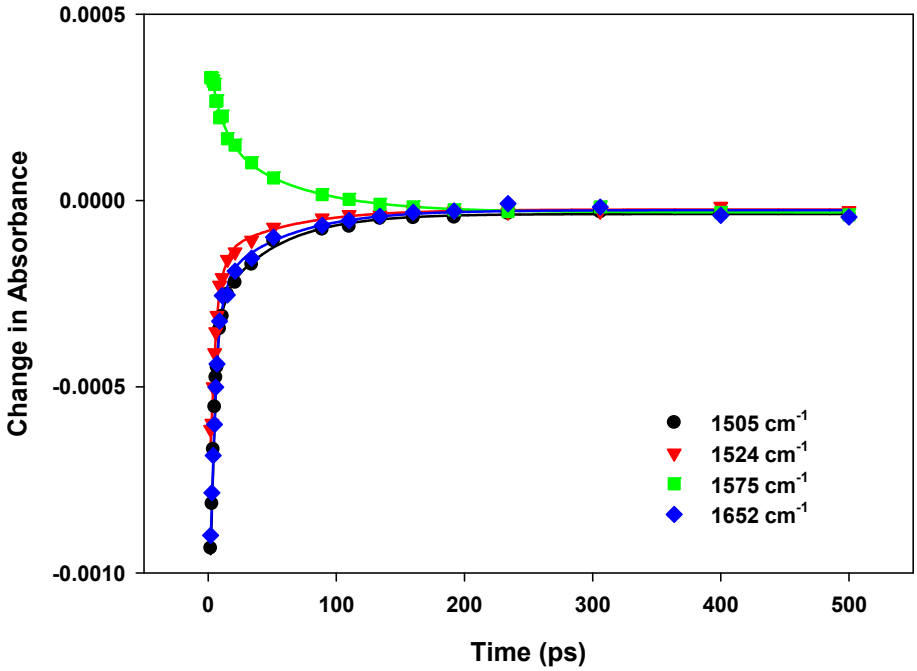

Figure S4. Kinetic analysis of 10 mM d(CpC) in 50 mM phosphate D_2O buffer (pH 7) at 1505, 1524, 1575 and 1652 cm^{-1}. Delays (ps): 2, 3, 4, 5, 6, 7, 9, 11, 15, 21, 34, 51, 70, 89, 110, 134, 160, 192, 234, 306, 400 and 500.

Data fitting

Table S1: Biexponential fitting parameters at 1574 cm^{-1}

DNA/RNA	τ_1	τ_2
5‘-dCMP	7 ± 2 ps (50%)	40 ± 5 ps (50%)
5‘-rCMP	7 ± 2 ps (57%)	52 ± 8 ps (43%)
d(CpC)	7 ± 2 ps (45%)	57 ± 9 ps (55%)
ss-dC_{30} pH 8.5	9 ± 2 ps (47%)	90 ± 10 ps (53%)
poly(rC)	9 ± 2 ps (44%)	85 ± 10 ps (56%)

Note: τ_1 is an overestimate of the true cooling lifetime, due to the spectral shifts observed at early delays (< 10 ps). Relative amplitudes depend on overlap of the vibrationally excited ground-state species at 1574 cm^{-1}.

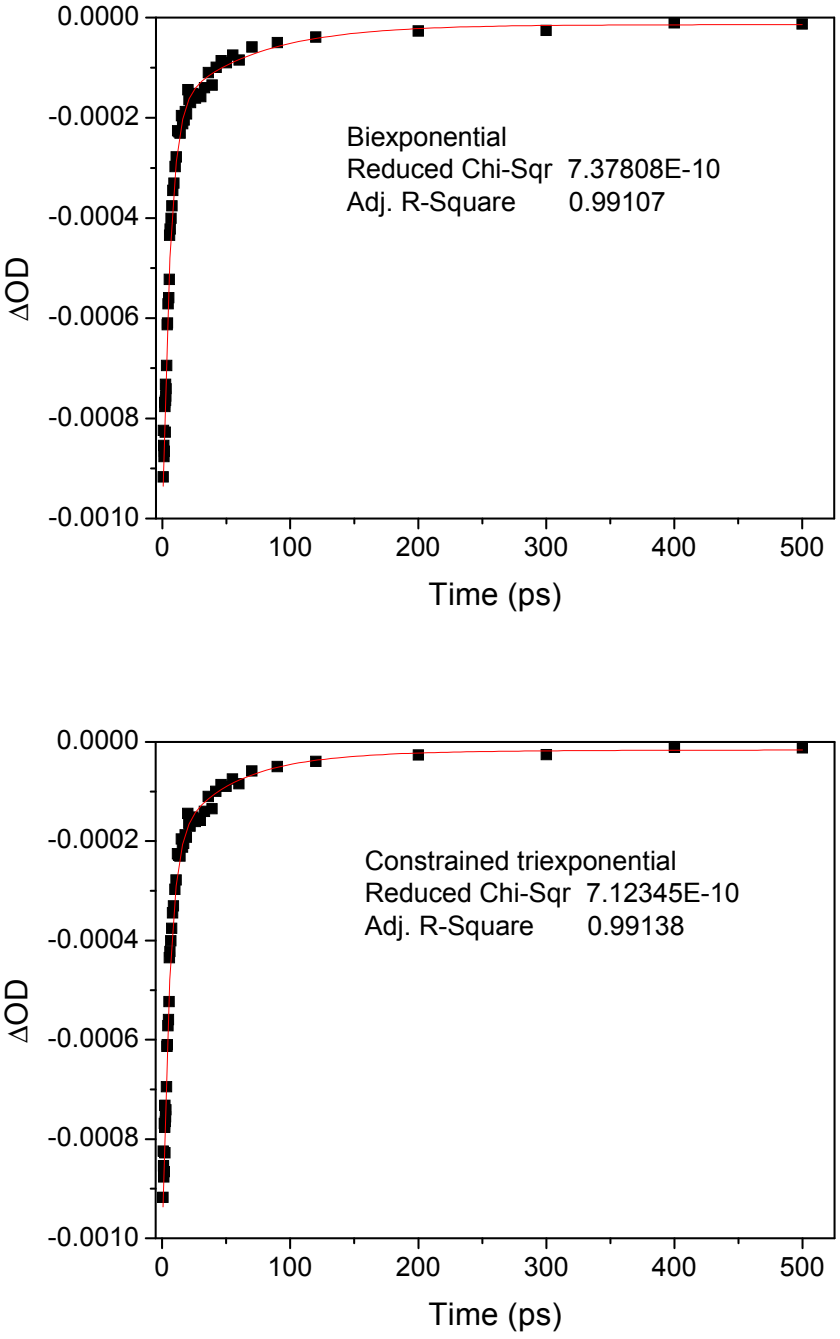

Figure S5: Comparison of biexponential and constrained triexponential fits to d(CpC) bleach recovery at 1649 cm^{-1}