Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supplementary Information

For

Time-resolved photoelectron imaging of the isolated deprotonated nucleotides

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Confidence Intervals

Confidence intervals for the extracted lifetimes have been produced using the support plane analysis technique.[fluor book] In this, the time constants are systematically varied over a range of points, and a global fit is performed with the time constants fixed, but all other parameters allowed to vary. The χ^2 value from the fit is then produced as a function of the time constants. A numerical confidence interval can be produced by noting the deviation in τ_i required to produce a statistically significant change in χ^2. The point of significant deviation for a 95% confidence interval is defined by:

$$\frac{\chi^2}{\chi^2_{min}} = 1 + \frac{p}{\nu} F(0.95, p, \nu)$$

where χ^2_{min} gives the χ^2 value at the global minimum of the fit, p is the number of parameters in the fit and ν is the degrees of freedom (total number of data points – p). All time constants are reported with the greater of the upper and lower bounds as the error. Qualitative insight can also be gained by viewing the map of $\chi^2 / \chi^2_{\min}$ as a function of τ, these are presented below. These maps allow the parameter space of acceptable solutions to be easily visualized.

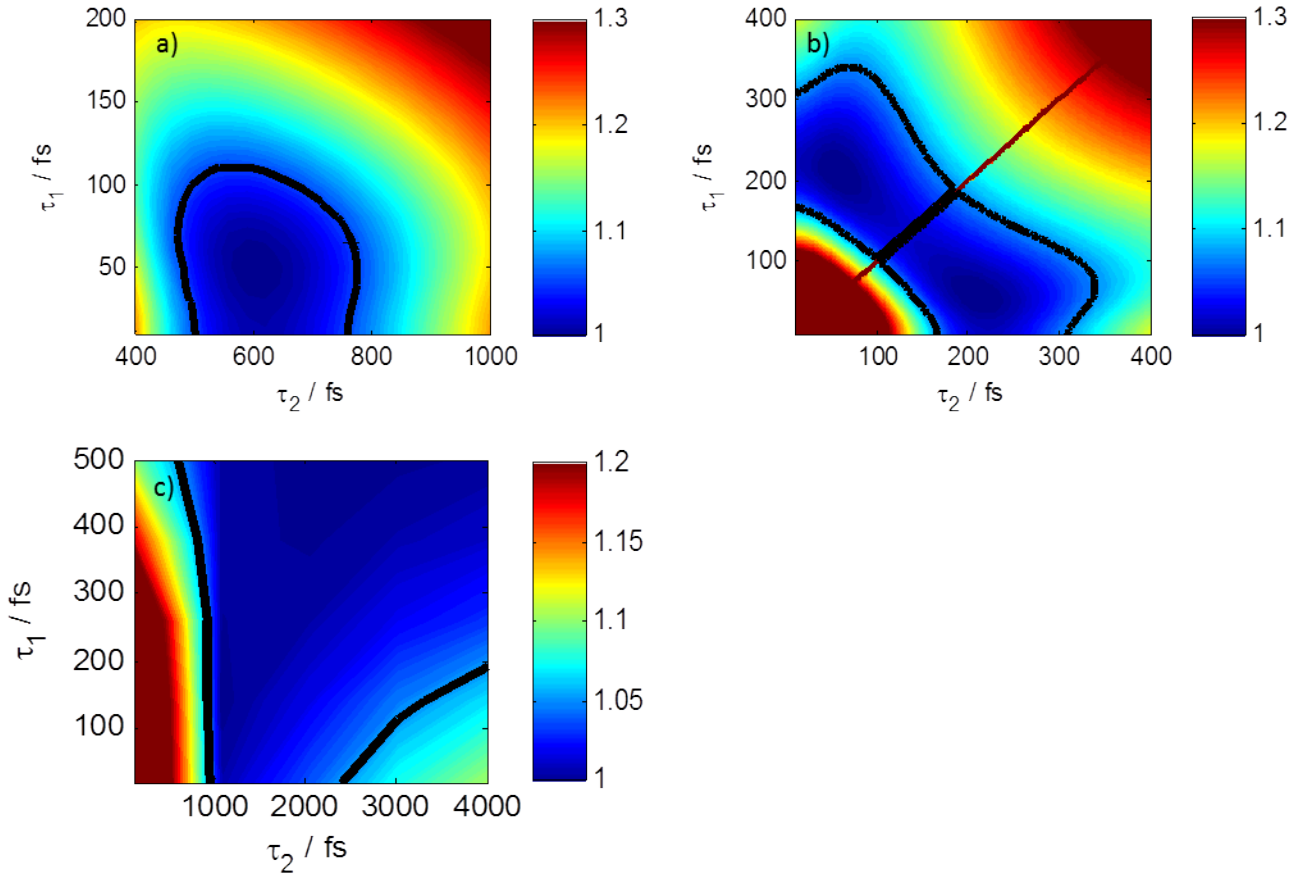

Figure S1 The $\chi^2 / \chi^2_{\min}$ map for the fits of a) dGMP$^-$, b) dTMP$^-$ and c) dCMP$^-$. At each point, the first two lifetimes were fit, and each other parameter was freely fit to minimize χ^2. The solid black line gives the region bounded by the 95% confidence interval. Note that the map of dCMP$^-$ is particularly shallow, hence the difficulty in making firm assignments about its dynamics.

Residuals of Fits

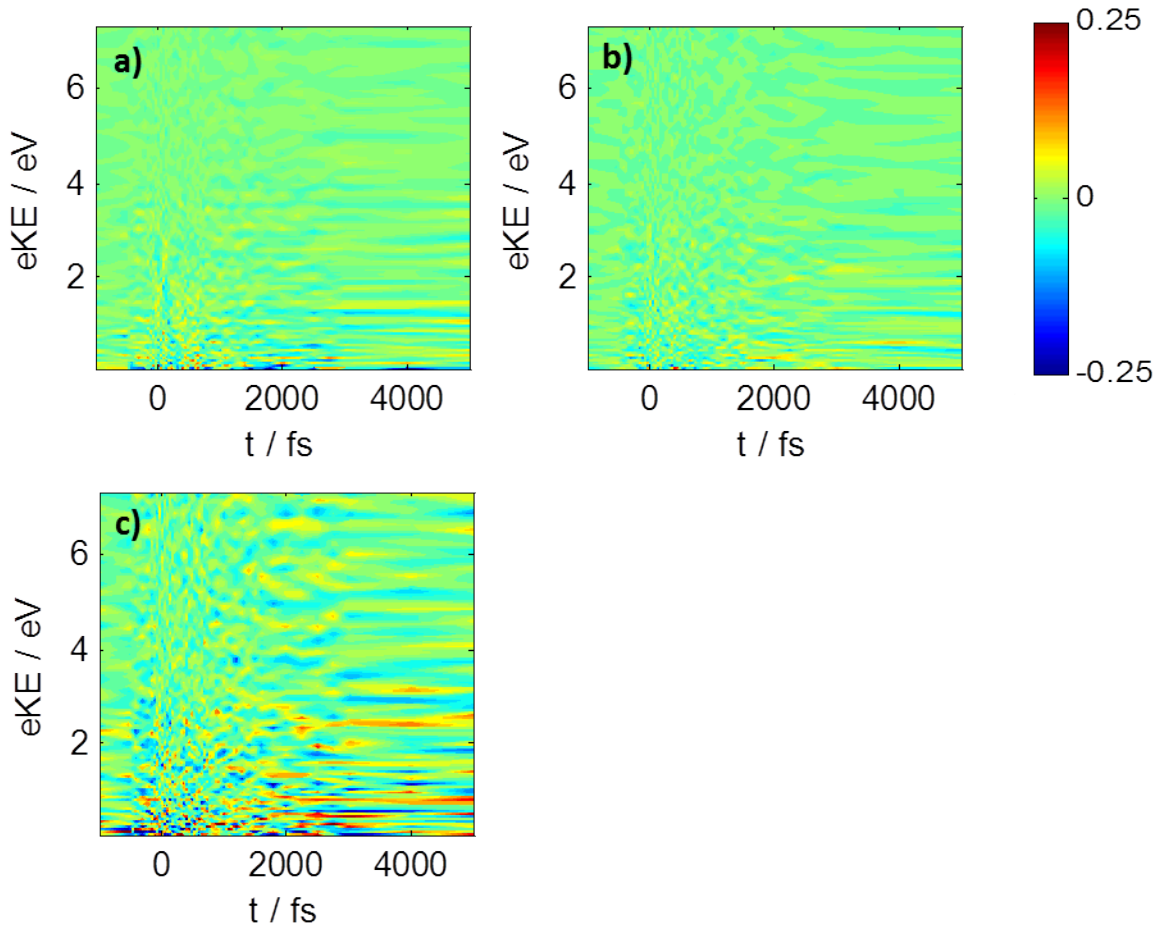

Figure 2S Residuals of fits for a) $dGMP^-$, b) $dTMP^-$ and c) $dCMP^-$. Note that the scale has been expanded ×2 compared to the data presented in the main text.

Photoelectron Angular Distributions

In addition to the producing a photoelectron *eKE* distribution, the velocity map imaging technique also provides information about photoelectron angular distributions. In the images of all three nucleotides presented in the main article, the observed angular distribution was essentially isotropic at all energies and delays. Angular distributions are much more sensitive to noise than *eKE* spectra, which are integrated over all angles, and so the scatter on the extracted anisotropy parameters is rather high. Within the error, there is no evidence of any anisotropic distributions. A delay invariant anisotropy parameter is consistent with dynamics all occurring on a single electronic excited state, though it is not an unambiguous identifier.

Energy slice normalized spectra

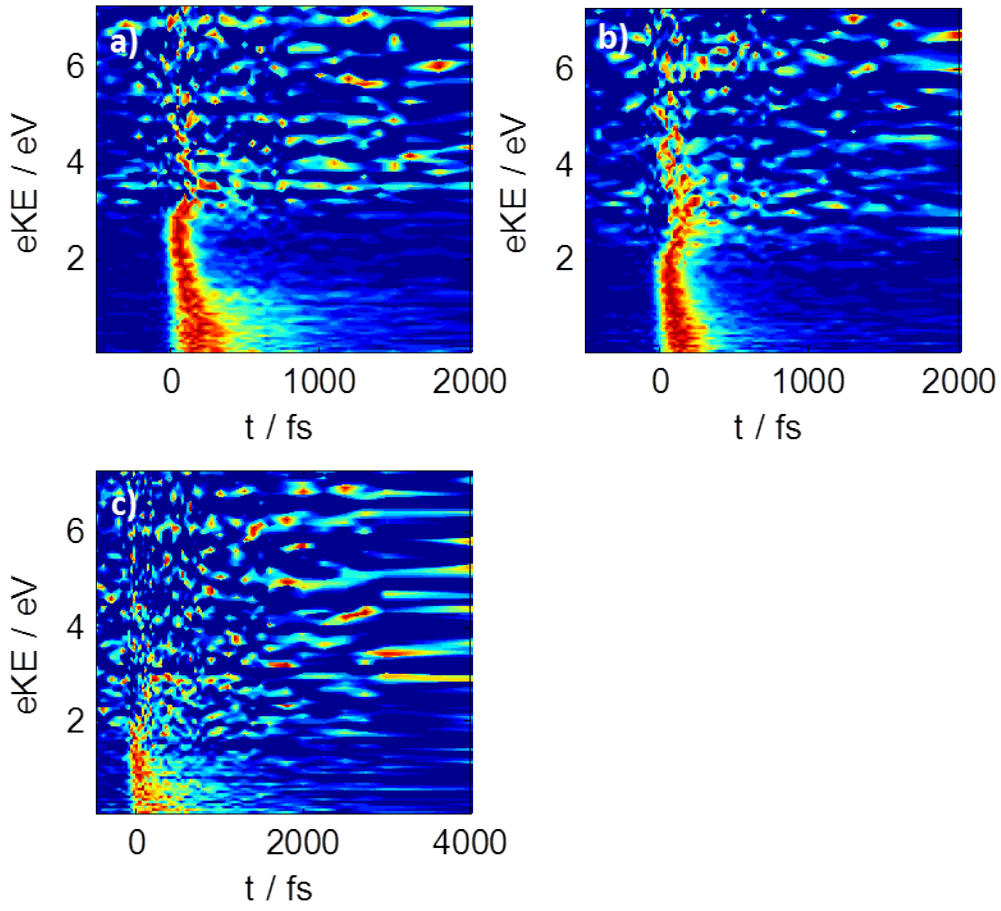

Figure S3 Energy slice normalized spectra for a) $dGMP^-$, b) $dTMP^-$ and c) $dCMP^-$. For each *eKE,* the data as a function of time have been normalized. The point of maximum intensity clearly shifts, indicating sequential dynamics. Two-photon signal is also very easily visualised in this way.