Supplementary information

S1. Time evolution of the excited state population

We assume Gaussian temporal profiles for the pump and probe pulses:

$$I(t) = \frac{A}{\sqrt{2\pi}\sigma}\exp\left(-\frac{1}{2}\frac{(t-t_0)^2}{\sigma^2}\right) \quad (1)$$

Neglecting any coherent effects, the population, $f(t)$, in any excited state, S_i, varies with time according to the formula :

$$\frac{df(t)}{dt} = \Sigma_{0i} I(t) - kf(t), \quad (2)$$

where Σ_{0i} is the excitation cross-section from the ground state to the electronically excited state S_i, and k is the total decay rate of the S_i state. This first order differential equation has a known solution:

$$f(t) = \exp(-kt)\int_{-\infty}^{t}\exp(kx)\Sigma_{0i}I(x)dx = \exp(-kt)\int_{-\infty}^{t}\exp(kx)\Sigma_{0i}\frac{A}{\sqrt{2\pi}\sigma}\exp\left(-\frac{1}{2}\frac{(x-t_0)^2}{\sigma^2}\right)dx$$

The convolution of the exponential and the Gaussian functions can be simplified and expressed in terms of the error function (see section S2), thus the time-evolution of the population in the excited state can be described by :

$$f(t) = \exp(-kt)\Sigma_{0i}\frac{A}{2}\exp\left(\frac{\sigma^2k^2}{2} + kt_0\right)\left(1 + erf\left(\frac{t - t_0 - \sigma^2k}{\sqrt{2}\sigma}\right)\right) \quad (3)$$

The decay rate, k, is related to the decay time, τ, by $k = 1/\tau$. By substituting for τ and setting $N = \Sigma_{0i}\, A/2$, we obtain equation (1) in the main paper:

$$f(t) = N\exp\left(\frac{\sigma^2}{2\tau^2} + \frac{t_0}{\tau} - \frac{t}{\tau}\right)\left(1 + erf\left(\frac{t - t_0 - \sigma^2}{\tau\sigma\sqrt{2}}\right)\right). \quad (4)$$

S2. Convolution of the exponential and Gauss functions

In order to solve the convolution integral,

$$\int_{-\infty}^{t}\exp(kx)\exp\left(-\frac{1}{2}\frac{(x-t_0)^2}{\sigma^2}\right)dx = \int_{-\infty}^{t}\exp\left(kx - \frac{1}{2}\frac{(x-t_0)^2}{\sigma^2}\right)dx, \quad (5)$$

the exponent in equation (5) has to be rearranged as shown below.

$$kx - \frac{1}{2}\frac{(x-t_0)^2}{\sigma^2} = -\frac{1}{2}\frac{(x-t_0)^2}{\sigma^2} + k(x-t_0) - kt_0 = -\frac{(x-t_0)^2 - 2\sigma^2k(x-t_0)}{2\sigma^2} + kt_0 =$$

$$= -\frac{(x-t_0)^2 - 2\sigma^2k(x-t_0) + \sigma^4k^2 - \sigma^4k^2}{2\sigma^2} + kt_0 = -\frac{(x - t_0 - \sigma^2k)^2}{2\sigma^2} + \frac{\sigma^2k^2}{2} + kt_0$$

To simplify this expression, a new variable, y, and an upper integration limit, t', is introduced as defined below:

$$y = \frac{x - t_0 - \sigma^2 k}{\sqrt{2}\sigma},\ dx = \sqrt{2}\sigma dy,\ t' = \frac{t - t_0 - \sigma^2 k}{\sqrt{2}\sigma} \tag{6}$$

Combining the above mathematical transformations gives the resultant integral:

$$\int_{-\infty}^{t} \exp\left(kx - \frac{1}{2}\frac{(x-t_0)^2}{\sigma^2} \right) dx = \exp\left(\frac{\sigma^2 k^2}{2} + kt_0 \right) \sqrt{2}\sigma \int_{-\infty}^{t'} \exp\left(-y^2\right) dy \tag{7}$$

Using the standard integral $\int_{-\infty}^{0} \exp\left(-y^2\right) dy = \frac{\sqrt{\pi}}{2}$, expression (7) can now be derived *via* the error function, $\int_{0}^{t} \exp\left(-y^2\right) dy = \frac{\sqrt{\pi}}{2} erf(t)$, as shown below :

$$\begin{aligned}
\int_{-\infty}^{t} \exp(kx) \exp\left(-\frac{1}{2}\frac{(x-t_0)^2}{\sigma^2} \right) dx &= \exp\left(\frac{\sigma^2 k^2}{2} + kt_0 \right) \sqrt{2}\sigma \int_{-\infty}^{t'} \exp\left(-y^2\right) dy \\
&= \exp\left(\frac{\sigma^2 k^2}{2} + kt_0 \right) \sqrt{2}\sigma \left(\int_{-\infty}^{0} \exp\left(-y^2\right) dy + \int_{0}^{t'} \exp\left(-y^2\right) dy \right) \\
&= \exp\left(\frac{\sigma^2 k^2}{2} + kt_0 \right) \sigma \left(\sqrt{\frac{\pi}{2}} + \sqrt{\frac{\pi}{2}} erf(t') \right) \\
&= \exp\left(\frac{\sigma^2 k^2}{2} + kt_0 \right) \sigma \sqrt{\frac{\pi}{2}} \left(1 + erf\left(\frac{t - t_0 - \sigma^2 k}{\sqrt{2}\sigma} \right) \right)
\end{aligned}$$