

# Photonic Crystal Fibre as an Optofluidic Reactor for the Measurement of Photochemical Kinetics with Sub-Picomole Sensitivity

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## Supplementary Information

### The Kinetic Model

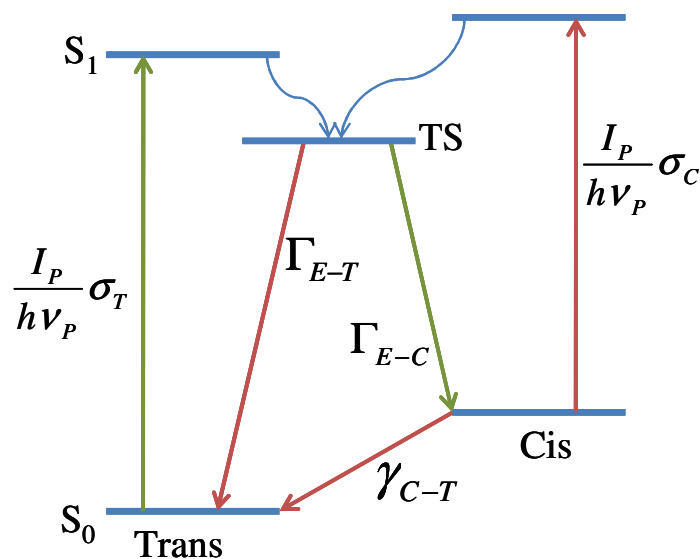
The experimental data are fitted numerically to a kinetic model, based on the excitation and decay processes shown in Figure S1. The photoisomerisation can be described by the three coupled rate equations, (1) to (3):

$$\frac{\partial n_T}{\partial t} = -\frac{I_p}{h\nu_p} \sigma_T n_T(t) + \Gamma_{E-T} n_E(t) + \gamma_{C-T} n_C(t) \quad (1)$$

$$\frac{\partial n_C}{\partial t} = -\frac{I_p}{h\nu_p} \sigma_C n_C(t) + \Gamma_{E-C} n_E(t) + \gamma_{C-T} n_C(t) \quad (2)$$

$$\frac{\partial n_E}{\partial t} = \frac{I_p}{h\nu_p} (\sigma_T n_T(t) + \sigma_C n_C(t)) - n_E(t) (\Gamma_{E-T} + \Gamma_{E-C}) \quad (3)$$

where  $n_{T,C,E}(t)$  are the normalised number densities in the *trans*, *cis* ground states and excited transition state;  $I_p$  and  $h\nu_p$  are the power density and photon energy of the pump light;  $\sigma_T$  and  $\sigma_C$  are the absorption cross-sections at the pump wavelength of the *trans* and *cis* isomers;  $\Gamma_{E-T}$  and  $\Gamma_{E-C}$  are the rate constants for decay from the excited transition state to the ground state *trans* and *cis* isomers;  $\gamma_{C-T}$  is the rate constant for thermal *cis* to *trans* isomerisation.



**Fig. S1.** Energy level diagram for the *cis-trans* isomerisation of azobenzenes, showing the processes and associated parameters used in the numerical model. Excitation of *trans* and *cis* isomers populates a common transition state (TS).

The model takes account of the pump/probe nature of the experiments, by including the thermal relaxation from *cis* to *trans* isomer during the periods when the excitation laser is off. Also, the long path length means that the reduction in excitation power along the length of the fibre, due to both absorption and intrinsic fibre losses, has to be taken into account. Integration is therefore carried out through both time and space, with the spatial loss being governed by the following equation:

$$I_p(z) = I_0 10^{\int_0^z \alpha(\xi) d\xi} \quad (4)$$

where  $I_0$  is the incident intensity,  $I_p$  is the intensity at position  $z$  along the fibre and  $\alpha(\xi)$  is the combined position-dependent attenuation due to fibre loss and molecular absorption

The incident intensity,  $I_0$ , is known (its measurement is straightforward since the whole of the irradiated sample is monitored). The absorption cross-sections of both the *trans* and *cis* isomers, along with the fibre loss per unit length, are also known parameters. The value for the *trans* isomer can be determined easily by measuring the absorption spectrum of a sample that has been left in the dark and is 100% *trans*. However, determination of the value for the *cis* isomer requires knowledge of the composition of the PSS. The composition of the PSS is obtained by monitoring the decrease in absorbance, on formation of the PSS, at a wavelength where only the *trans* isomer absorbs; in the present case, this corresponds to the maximum of the measured absorption spectrum.

The value of the thermal isomerisation rate constant,  $\gamma_{C-T}$ , is measured independently and is a fixed parameter in the photoisomerisation model.

Applying the model to the temporal evolution of the absorbance, measured experimentally during the photoinduced conversion of the all-*trans* sample to the photostationary state, yields the ratio of  $\Gamma_{E-T}$  and  $\Gamma_{E-C}$ . The quantum yield for *trans* to *cis* photoisomerisation can then be determined.