

Supplementary Materials for

A deep UV trigger for ground-state ring-opening dynamics of 1,3-cyclohexadiene

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This PDF file includes:

Section S1. Anisotropic and isotropic scattering decomposition

Section S2. Kinetics fit

Section S3. Separating HT rotamers

Fig. S1. The time-resolved anisotropic scattering signal for CHD excited at 200 nm.

Fig. S2. The residuals of the kinetics fit, divided into temporal regions as shown in Fig. 3 of the main text.

Table S1. Criteria for fitting the HT rotamers.

Section S1. Anisotropic and isotropic scattering decomposition

The anisotropic and isotropic scattering were separated using a standard method.(23) The decomposition equation used was:

$$\% \Delta I_{total}(q, t) = \frac{1}{2} \left(3 \left(\cos(\phi) \sqrt{1 - \left(\frac{\lambda q}{4\pi} \right)^2} \right)^2 - 1 \right) P_{aniso}(q, t) + P_{iso}(q, t)$$

Where ϕ is the azimuthal scattering angle, and $P_{iso}(q, t)$ and $P_{aniso}(q, t)$ are the isotropic and anisotropic scattering contributions, respectively. The anisotropic scattering signal is shown in fig. S1.

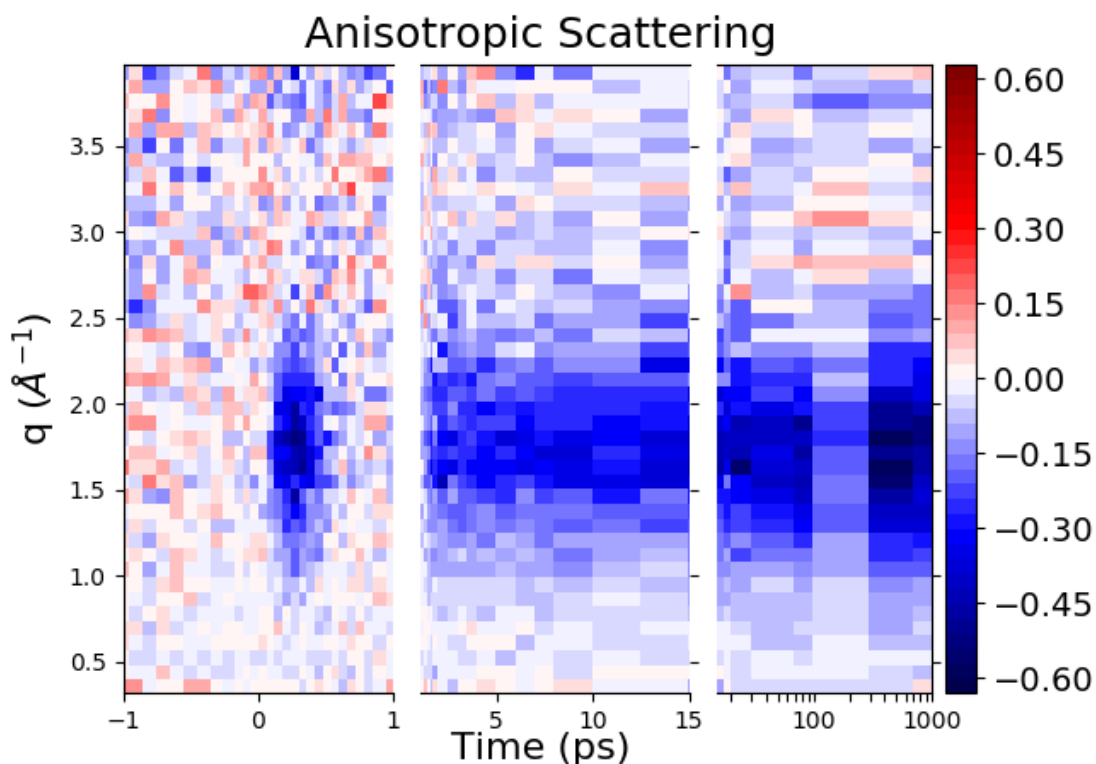


Fig. S1. The time-resolved anisotropic scattering signal for CHD excited at 200 nm. The anisotropic arises shortly after the excitation, then dephases in about 500 fs before rephasing starting at a time delay of about 2 ps.

Section S2. Kinetics fit

The kinetics equations (Equations 2) were convoluted with a gaussian instrument function:

$$g(t) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{t-t_0}{\sigma}\right)^2}$$

The analytical forms of these equations can be found:

$$e^{-k(t-t_0)} \otimes g(t) = \left[\frac{1}{2} + \frac{1}{2} \text{Erf} \left(\frac{(t-t_0) - \sigma^2 k}{\sqrt{2}\sigma} \right) \right] \times e^{-k(t-t_0) + k^2 \sigma^2 / 2}$$

$$H(t-t_0) \otimes g(t) = \frac{1}{2} \text{Erf} \left(\frac{(t-t_0)}{\sqrt{2}\sigma} \right) + \frac{1}{2}$$

Where $H(t)$ is the Heaviside function. Thus the convolutions of Equations 2 with the instrument function are as follows:

$$[CHD^*](t) = e^{-k_1(t-t_0)} \otimes g(t)$$

$$[CHD_{hot}](t) = A_1 [e^{-k_1(t-t_0)} \otimes g(t) - e^{-(k_2+k_{-2})(t-t_0)} \otimes g(t)] + B [H(t-t_0) \otimes g(t) - e^{-(k_2+k_{-2})(t-t_0)} \otimes g(t)]$$

$$[HT_{hot}](t) = A_2 [e^{-k_1(t-t_0)} \otimes g(t) - e^{-(k_2+k_{-2})(t-t_0)} \otimes g(t)] + B [H(t-t_0) \otimes g(t) - e^{-(k_2+k_{-2})(t-t_0)} \otimes g(t)]$$

Where t is time, t_0 is time of the UV excitation, and σ is the gaussian width, found to be 116 ± 30 fs.

To show the quality of the kinetics fit, the residuals are plotted in fig. S2. These residuals show that the residuals are small compared to the magnitude of the signal. There is no systematic variation of the signal that the kinetic fit does not capture. This suggests that dynamic motions between hexatriene isomers are not apparent in this experiment.

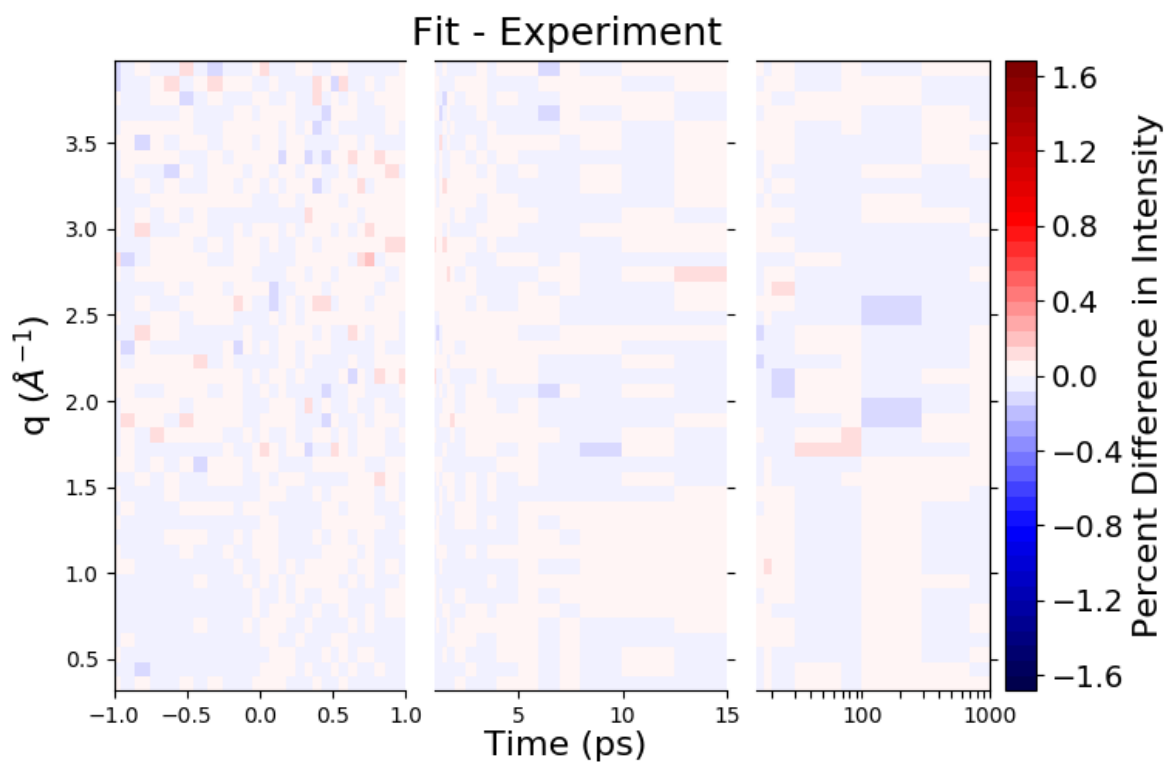
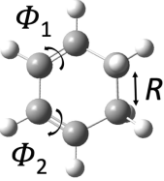
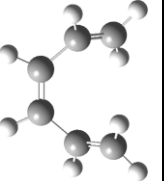
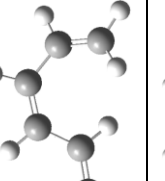
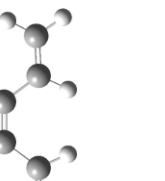


Fig. S2. The residuals of the kinetics fit, divided into temporal regions as shown in Fig. 3 of the main text. Plotted is the difference between the fit results and the experimental data as a function of scattering vector q and the delay time. The color scale matches that of Figure 3, top.

Section S3. Separating HT rotamers

After the HT conformers are calculated as described in the Experimental and Computational Methods section, the HT conformers are divided into cZc, cZt, and tZt rotamers based on the criteria indicated in Table S1, adapted from Wolf *et al.*(5) In the Table, R is the terminal carbon C5-C6 distance, while Φ_1 and Φ_2 are the torsional angles about the HT single bonds that indicate the *cis* and *trans* conformations.

Table S1. Criteria for categorizing HT conformers.

CHD	cZc-HT	cZt-HT	tZt-HT
			
$R < 1.8\text{\AA}$	$R > 1.8\text{\AA}$	$R > 1.8\text{\AA}$	$R > 1.8\text{\AA}$
$ \Phi_1 \leq 90^\circ$	$ \Phi_1 \leq 90^\circ$	$ \Phi_1 \leq 90^\circ$	$ \Phi_1 \geq 90^\circ$
$ \Phi_2 \leq 90^\circ$	$ \Phi_2 \leq 90^\circ$	$ \Phi_2 \geq 90^\circ$	$ \Phi_2 \geq 90^\circ$