Supporting Information for: Effects of ring-strain on the ultrafast photochemistry of cyclic ketones

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Figure S1. Normalised UV/Vis absorption spectra of cyclobutanone (black), cyclopentanone (red) and cyclohexanone (blue) in cyclohexane. The concentrations of the solutions used for the measurements were 0.25 M, and the cuvette pathlength was 2 mm.



Figure S2. Example of the decomposition of TEA spectra of a cyclobutanone solution in cyclohexane using early and medium time (ET and MT) basis spectra corresponding to the experimental spectra measured at $\Delta t = 0.2$ and 50 ps, respectively. The TEA spectra were obtained at an excitation wavelength of 312 nm, and the decomposition was performed in the KOALA program. The sample spectra plotted were taken at three different time delays: 0.85 ps (top), 30 ps (middle) and 400 ps (bottom). In each case, the black solid line is the experimental spectrum, and the violet dashed line is the best fit. ET and MT basis functions are shown as red and blue solid lines respectively. Decomposition of cyclobutanone spectra obtained at shorter excitation wavelengths ($\lambda_{exc} = 255$, 281 and 290 nm) required use of only a single (ET) basis function.



Figure S3. Example of the decomposition of TEA spectra of a cyclopentanone solution in cyclohexane using early and late time (ET and LT) basis spectra corresponding to experimental spectra measured at $\Delta t = 0.2$ and 1300 ps, respectively. The TEA spectra were obtained at an excitation wavelength of 281 nm, and the decomposition was performed in the KOALA program. The sample spectra plotted were taken at three different time delays: 1.8 ps (top), 70 ps (middle) and 1000 ps (bottom). In each case, the black solid line is the experimental spectrum, and the violet dashed line is the best fit. ET and LT basis functions are shown as red and blue solid lines respectively.



Figure S4. Example of the decomposition of TEA spectra of a cyclohexanone solution in cyclohexane using early and medium time (ET and MT) basis spectra which correspond to experimentally measured spectra at $\Delta t = 0.3$ and 100 ps, respectively. The TEA spectra were obtained at an excitation wavelength of 312 nm, and the decomposition was performed in the KOALA program. The sample spectra plotted were taken at three different time delays: 1 ps (top), 8.5 ps (middle) and 80 ps (bottom). In each case, the black solid line is the experimental spectrum, and the violet dashed line is the best fit. ET and MT basis functions are shown as red and blue solid lines respectively.

Cyclobutanone

Pump wavelength	τ ₁		τ ₂		τ_1 / τ_2		
(nm)	Amplitude	error	Amplitude	error	Amplitude		error
255	0.57	0.01	0.16	0.01		3.56	0.18
281	0.69	0.01	0.30	0.01		2.30	0.07
290	0.68	0.02	0.31	0.01		2.19	0.08
312	0.56	0.01	0.57	0.01		0.98	0.02

Table S1. Amplitudes of the fastest (τ_1 = 0.65 ± 0.02 ps) and intermediate (τ_2 = 7.0 ± 0.2 ps) time components of the tri-exponential decays of intensity of ET basis function observed by decomposition of TEA spectra of photoexcited cyclobutanone. Data are shown for four different UV excitation wavelengths. τ_1/τ_2 ratios show that the contribution of the fastest time constant decreases with longer excitation wavelengths.



Figure S5. Left-hand column: TEA spectra of cyclopentanone in cyclohexane, obtained with excitation wavelengths of 255 nm, 281 nm, 290 nm and 312 nm (from top to bottom). The spectra were obtained at different pump-probe time delays, as indicated by the inset colour key. Right-hand column: kinetics of excited state cyclopentanone relaxation obtained by analysis of TEA spectra. Red and blue symbols are intensities obtained from the fits to ET and LT basis functions. The solid lines are a global fit to tri-exponential functions, yielding components with common time constants of $\tau_1 = 0.95 \pm 0.03$ ps, $\tau_2 = 8.5 \pm 0.3$ ps and $\tau_3 = 600 \pm 100$ ps.

Cyclopentanone

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ength	ngth τ ₁		τ ₂		τ_1/τ_2	
(nm)	Amplitude	error	Amplitude	error	Amplitude	error
255	0.61	0.01	0.23	0.01	2.65	0.08
281	0.71	0.01	0.38	0.01	1.87	0.05
290	0.87	0.02	0.57	0.01	1.53	0.04
312	0.46	0.01	0.60	0.01	0.77	0.02

Table S2. Amplitudes of the fastest ($\tau_1 = 0.95 \pm 0.03$ ps) and intermediate ($\tau_2 = 8.5 \pm 0.3$ ps) time components of the tri-exponential decays of ET basis function intensity observed by decomposition of TEA spectra of photoexcited cyclopentanone. Data are shown for four different UV excitation wavelengths. τ_1/τ_2 ratios show that the contribution of the fastest time constant decreases with longer excitation wavelengths.



Figure S6. Left-hand column: TEA spectra of cyclohexanone in cyclohexane, obtained with excitation wavelengths of 255 nm, 281 nm, 290 nm and 312 nm. The spectra were obtained at different pump-probe time delays, as indicated by the inset colour key. Right-hand column: kinetics of excited state cyclohexanone relaxation obtained by analysis of TEA spectra measured at time delays up to 100 ps. Red and blue symbols are intensities obtained from the fits to ET and MT basis functions. The solid lines are a global fit to bi-exponential functions, yielding components with common time constants of $\tau_1 = 1.02 \pm 0.03$ ps and $\tau_2 = 8.9 \pm 0.3$ ps.

Cyclohexanone

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ength	τ ₁		τ ₂		τ_1/τ_2	
(nm)	Amplitude	error	Amplitude	error	Amplitude	error
255	0.50	0.01	0.3	0.01	1.67	0.06
281	0.69	0.01	0.44	0.01	1.57	0.04
290	0.66	0.01	0.49	0.01	1.35	0.03
312	0.54	0.02	0.57	0.01	0.95	0.04

Table S3. Amplitudes of the fastest ($\tau_1 = 1.02 \pm 0.03 \text{ ps}$) and intermediate ($\tau_2 = 8.9 \pm 0.3 \text{ ps}$) time components of the tri-exponential decays of ET basis function intensity observed by decomposition of TEA spectra of photoexcited cyclohexanone. Data are shown for four different UV excitation wavelengths. τ_1/τ_2 ratios show that the contribution of the fastest time constant decreases with longer excitation wavelengths.

Figure S7. Example of the decomposition of TVA spectra obtained in the ketene region for a UV-excited cyclobutanone solution in cyclohexane. The decomposition used a Gaussian function and a Lorentzian function with centres that shift with time. The TVA spectra were obtained at an excitation wavelength of 281 nm, and the decomposition was performed in the KOALA program. The sample spectra plotted were taken at three different time delays: 0.5 ps (top), 14 ps (middle) and 250 ps (bottom). In each case, the black solid line is the experimental spectrum, and the violet dashed line is the best fit. The Gaussian function (representing a broad absorption by vibrationally hot ketene molecules) and the Lorentzian function (for the vibrationally thermalized ketene peak) are shown as blue and red solid lines respectively.

Figure S8. Transient vibrational absorption spectra obtained in the ketene region for solutions of cyclobutanone in cyclohexane photoexcited at λ_{exc} = 255 nm (left panel) and λ_{exc} = 312 nm (right panel). The TVA spectra shown correspond to a pump-probe time delay of 1200 ps. The peak at ~2140 cm⁻¹ is indicative of ketene photoproduct formation, but the weak bands suggest low quantum yields for this pathway at these excitation wavelengths.

Figure S9. Transient vibrational absorption spectra and decay kinetics of cyclobutanone in cyclohexane photoexcited at λ_{exc} = 281 nm. Left panel: TVA spectra obtained at time delays from 0.2 – 1200 ps, as indicated by the inset colour key. The parent molecule has a strong absorption centred at ~1780 cm⁻¹. Right panel: Time-dependence of the integrated intensity of the transient absorption by cyclobutanone, extracted from the TVA spectra by integrating spectral absorbance from 1760-1770 cm⁻¹ (red circles), and a tri-exponential fit to the data (solid line).

Figure S10. Transient vibrational absorption spectra and decay kinetics of cyclohexanone in cyclohexane photoexcited at λ_{exc} = 281 nm. Left panel: TVA spectra obtained at time delays from 0.2 – 1200 ps, as indicated by the inset colour key. The parent molecule has a strong absorption centred at ~1710 cm⁻¹. Right panel: Time-dependence of the integrated intensity of the transient absorption by cyclohexanone, extracted from the TVA spectra by integrating spectral absorbance from 1690-1700 cm⁻¹ (red circles), and a tri-exponential fit to the data (solid line).

Figure S11. Transient vibrational absorption spectra and decay kinetics of cyclobutanone in cyclohexane photoexcited at λ_{exc} = 281 nm. Left panel: TVA spectra obtained at time delays from 0.2 – 1200 ps, as indicated by the inset colour key. Right panel: decay of the cyclobutanone ESA, extracted from the TVA spectra as described in the main text (red circles) and a biexponential fit to the data (solid line) with time constants of 0.7 and 7 ps.

Figure S12. Transient vibrational absorption spectra and decay kinetics of cyclohexanone in cyclohexane photoexcited at λ_{exc} = 281 nm. Left panel: TVA spectra obtained at time delays from 0.2 – 1200 ps, as indicated by the inset colour key. Right panel: decay of the cyclohexanone ESA, extracted from the TVA spectra as described in the main text (red circles) and a tri-exponential fit to the data (solid line) with time constants of 1, 9 and 1300 ps.