Electronic Supplementary Information: Broadband ultrafast photoprotection by oxybenzone ccross the UVB and UVC spectral regions

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1. Global Fits: $355 \leq \lambda \leq 415$ nm

To understand the dynamical process(es) involved across the collected transient electronic absorption (TEA) spectra, global fitting is implemented. As discussed in the corresponding communication, two features dominate the TEA spectra of oxybenzone (OB) in either cyclohexane or methanol at both 287 and 243 nm pump excitation wavelengths at early pump-probe time delays. The first is an intense peak centred at 366 nm, the second is a broad absorption stretching out to ~650 nm. The global fit comprises two non-convolved exponential functions with lifetimes τ_1 and τ_2. In all cases, the instrument response is removed from the fit by the exclusion of early pump-probe delay times (Δt) with $\Delta t < 250$ fs for 287 nm excitation and $\Delta t < 300$ fs for 243 nm excitation. Convolution with our instrument response function was deemed unnecessary given that the dynamics being modelled are far-removed from the initial dynamics around time zero.

The TEA spectra, global fits, and residual plots are shown for OB-cyclohexane after 287 nm irradiation in Fig. S1A-C respectively. Similarly, for OB-methanol after 287 nm excitation, the corresponding TEA spectra, global fits, and residual plots are shown in Fig. S1D-F. The lifetimes extracted from these global fits are summarised in Table S1. The uncertainties reported along with these lifetimes are determined from support plane analysis [1, 2, 3] and represent a 95 % confidence interval (2σ), see Fig. S3 [4]. The contours shown in black encompass values of τ_1 and τ_2 which return a goodness of fit, χ^2, which is within 2σ, thus, the largest deviation from the values determined by the global fit, which returns the value χ^2_{min}, are an upper bound to the uncertainties on the lifetimes and are the uncertainties reported throughout. Further details regarding the global fitting procedure, as well as the fitting algorithm and error analysis, can be found in Section 4 and ref [5].

An analogous treatment is applied to all 243 nm excitation measurements for OB-cyclohexane and OB-methanol, see Fig. S2A-C and Fig. S2D-F respectively. The only alteration in the analysis is the inclusion of a solvent response in the global fitting procedure as an additional non-convoluted exponential with a fixed lifetime of ~400 ps for cyclohexane and ~3 ns for methanol. These values are determined from the global fitting of solvent only scans at 243 nm excitation. We note the actual value of the solvent response is somewhat

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Table S1 Summary of the lifetimes of the observed dynamical processes of oxybenzone when excited at 325 nm (UVA), 287 nm (UVB) and 243 nm (UVC) regions. UVA measurements are taken from reference [1].

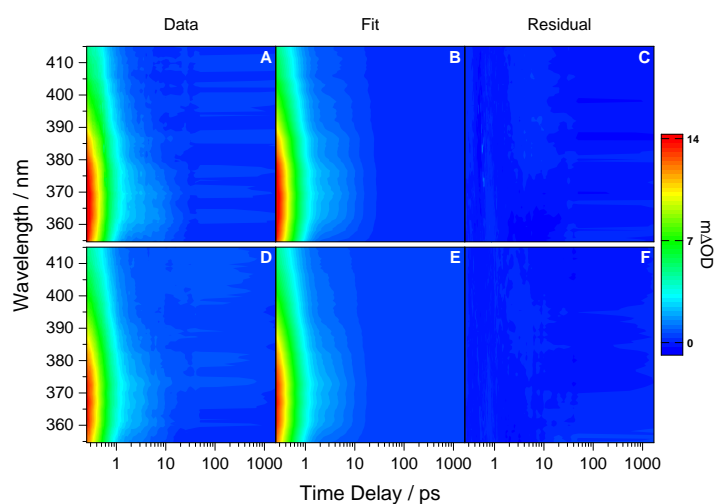| Excitation		Cyclohexane		Methanol	
Region	λ / nm	τ_1 / fs	τ_2 / ps	τ_1 / fs	τ_2 / ps
UVA	325	375 ± 13	7.8 ± 2.8	368 ± 13	4.9 ± 1.9
UVB	287	391 ± 12	8.6 ± 2.7	382 ± 8	6.0 ± 1.0
UVC	243	392 ± 10	11.0 ± 4.4	371 ± 9	7.8 ± 1.8

Fig. S1 Global fit after 287 nm excitation of OB-cyclohexane (A-C) and OB-methanol (D-F). (A and D) Data in the wavelength region of 355-415 nm with resultant global fit (B and E). (C and F) The residuals between the experimental data (A and D) and fitted values (B and E).

unimportant as it behaves as a long-lived baseline offset in the TAS. For example, in cyclohexane, a solvent response with lifetime >300 ps used in the global fit does not change the values of τ_1 and τ_2 from those reported, similarly for a solvent lifetime >2 ns for methanol. The global fitted values determined for 243 nm measurements are summarised in Table S1.
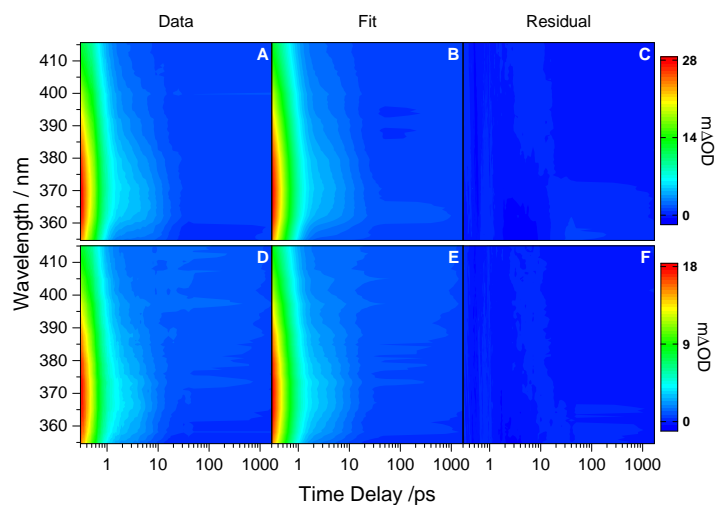
Fig. S2 Global fits after 243 nm excitation of OB-cyclohexane (A-C) and OB-methanol (D-F). (A and D) Data in the wavelength region of 355-415 nm with resultant global fit (B and E). (C and F) The residuals between the experimental data (A and D) and fitted values (B and E).
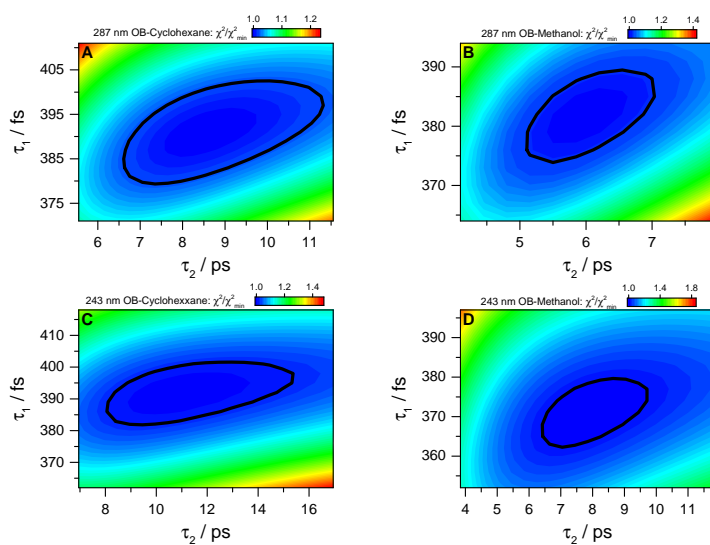

Fig. S3 (A) 287 nm OB-cyclohexane. The uncertainties are determined from the largest deviation from the global fitted values of τ_1 and τ_2 which lie on the edge of the 95 % confidence interval (shown in black), determined from support plane analysis [2, 3]. Identical analysis is applied to determine the uncertainties from global fitting 287 nm OB-methanol (B), 243 nm OB-cyclohexane (C) and 243 nm OB-methanol (D).

2. Global Fits: $415 < \lambda \leq 650$ nm

As mentioned in Section 1, a flat broad absorption extending out to $\sim$650 nm dominates the TEA spectra for both 287 nm and 243 nm excitation. We employ global fitting in the

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range of 415-650 nm to model the dynamical processes involved for OB-cyclohexane and OB-methanol for 287 nm excitation (Fig. S4A-F) and analogously, for OB-cyclohexane and OB-methanol for 243 nm excitation (Fig. S5A-F). One non-convoluted exponential function is required to recover the dynamics observed in the TEA spectra (and an additional solvent response for UVC measurements as described in Section 1). The lifetime of this exponential in all experiments is summarised in Table S2. We note that the lifetime closely mirrors that of the τ_1 process in the spectral region 355-415 nm. A small contribution of the longer τ_2 process, as described for the 355-415 nm region, exists and artificially increases the lifetime as determined from the single exponential fit. The uncertainties reported have been calculated in an analogous way to that described in Section 1 and are shown in Fig. S6.

Table S2 Summary of the lifetimes of observed dynamical processes of oxybenzone when excited at 325 nm (UVA), 287 nm (UVB) and 243 nm (UVC) regions in the spectral region 415-650 nm. UVA measurements are taken from reference [1]. Here, for succinctness, C=Cyclohexane and M=Methanol.

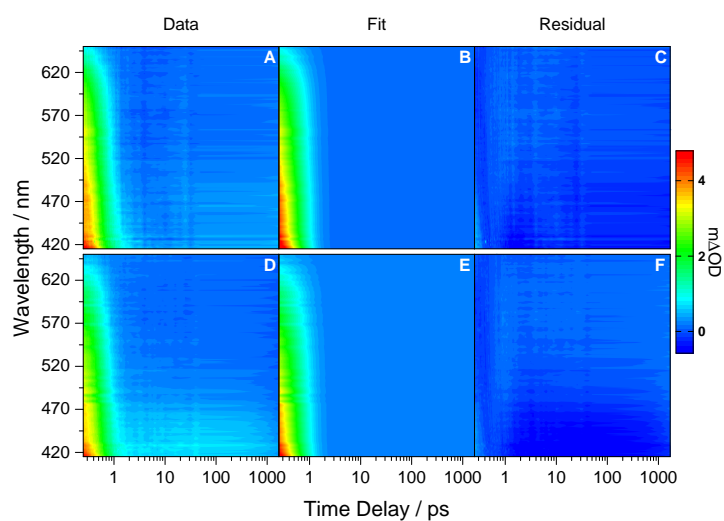|	UVA		UVB		UVC	
	C	M	C	M	C	M
τ / fs	493 ± 11	462 ± 14	468 ± 12	474 ± 16	448 ± 10	394 ± 8

Fig. S4 Global fits after 287 nm excitation of OB-cyclohexane (A-C) and OB-methanol (D-F). (A and D) Data in the wavelength region of 415-650 nm with resultant global fit (B and E). (C and F) The residuals between the experimental data (A and D) and fitted values (B and E).
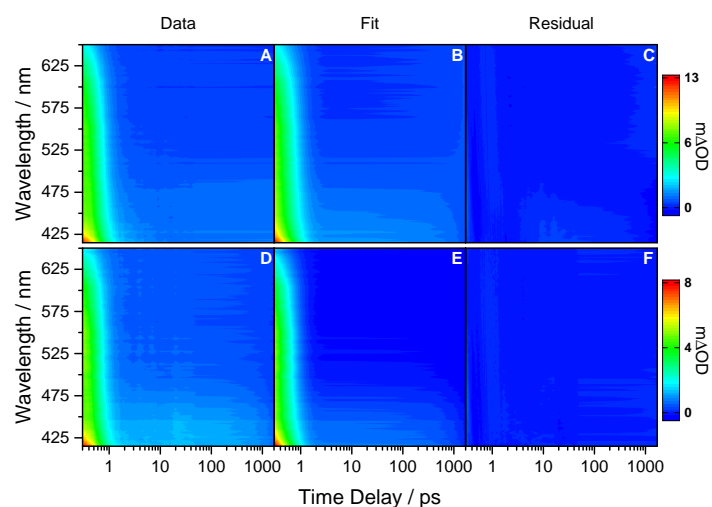
Fig. S5 Global fits after 243 nm excitation of OB-cyclohexane (A-C) and OB-methanol (D-F). (A and D) Data in the wavelength region of 415-650 nm with resultant global fit (B and E). (C and F) The residuals between the experimental data (A and D) and fitted values (B and E).
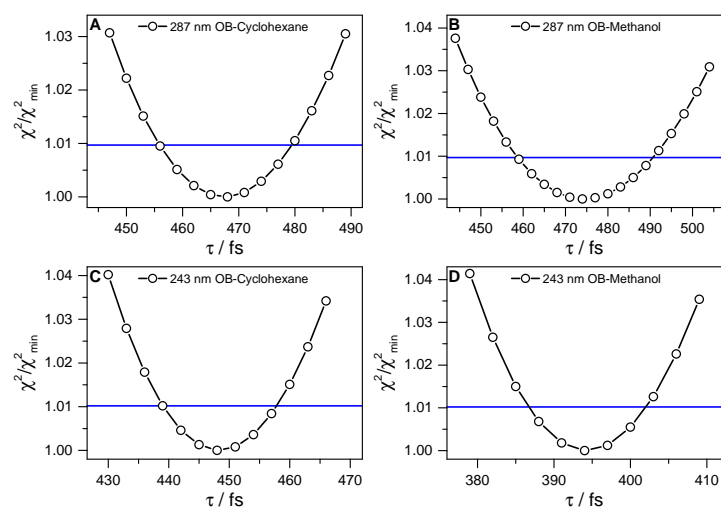

Fig. S6 (A) 287 nm OB-cyclohexane. The uncertainties are determined from the largest deviation from the global fitted values of τ which intersect with the 95 % confidence interval (horizontal blue line), determined from support plane analysis [2, 3]. Identical analysis is applied to determine the uncertainties from global fitting 287 nm OB-methanol (B), 243 nm OB-cyclohexane (C) and 243 nm OB-methanol (D).

3. Solvent response: 243 nm cyclohexane and methanol

As described in Section 1, solvent only TAS were acquired to calculate the response across the region $355 \leq \Delta\lambda \leq 650$ nm. The solvent only scans are shown in Fig. S7A and D along with the globally fitted values (Fig. S7B and E) and residuals plots (Fig. S7C and F)

for cyclohexane and methanol respectively. A single non-convoluted exponential function is required to recover the dynamics in the TAS, excluding time delays <1 ps in cyclohexane and <1.6 ps methanol. The lifetimes for the solvent response are determined to be $\sim$400 ps for cyclohexane and $\sim$3 ns for methanol. These lifetimes were used in the corresponding global fits as described in Sections 1 and 2.
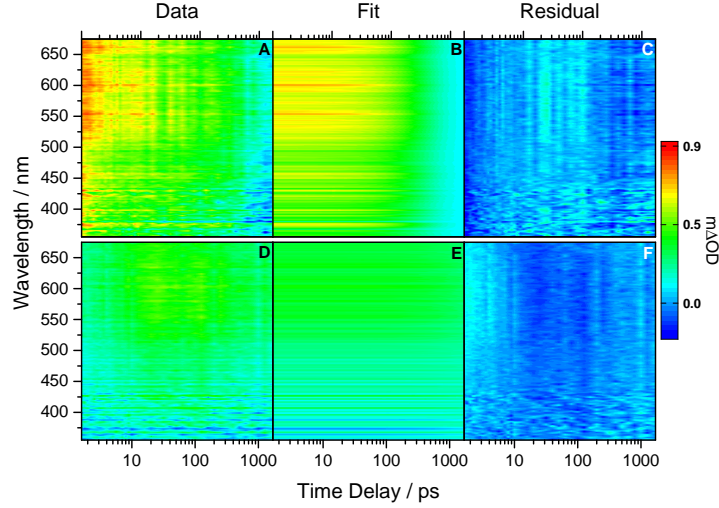

Fig. S7 Global fit after 243 nm excitation of cyclohexane only (A-C) and methanol only (D-F). (A and D) Data in the wavelength region of 355-650 nm with resultant global fit (B and E). (C and F) The residuals between the experimental data (A and D) and fitted values (B and E).

4. Global fit uncertainties

Support plane analysis is used to calculate the uncertainties on the global fitted values reported in Tables S1 and S2, see references [2, 3, 5] for more details.

The goodness of fit, χ^2, of the lifetimes reported (τ_1 and τ_2) which together parameterise the raw TEA data, is a global minimum with value χ^2_{min}. The lifetimes used in the global fit are varied in a systematic manner to sample the goodness of fit in the local parameter space surrounding this minimum, which return the values $\chi^2(\tau_1, \tau_2)$. The ratio $\frac{\chi^2(\tau_1,\tau_2)}{\chi^2_{min}}$ is then determined, thus the global minimum is given by $\frac{\chi^2(\tau_1,\tau_2)}{\chi^2_{min}} = 1$. For all fitting values which are not a global minimum, the ratio is always > 1. A confidence interval at the N level ($N = [0,1]$) is defined as:

$$\frac{\chi^2(\tau_1, \tau_2)}{\chi^2_{min}} = 1 + \frac{p}{\nu}\mathsf{F}\left(N, p, \nu\right), \tag{1}$$

where p is the number of parameters in the global fit, ν is the number of degrees of freedom and F is the inverse cumulative F-distribution function. Thus, the upper bound on the uncertainty for each varied parameter is the value which results in the largest deviation from the global fitted values whilst satisfying equation 1. Throughout this communication, all

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uncertainties are reported to a 95% level ($N = 0.95$). Qualitatively, these error bounds are shown in Fig. S3 and Fig. S6. In general, the uncertainties obtained from support plane analysis are an over estimate.

5. 366 nm and 380 nm transients

Raw 366 nm and 380 nm transients for OB-cyclohexane and OB-methanol for both UVB and UVC excitations (Fig. S8) are fitted with a bi-exponential function with lifetimes summarised in Table S3. As with the global fitting procedure described in Sections 1 and 2, UVB transients were fitted over the time delays, 250 fs $\leq \Delta\tau \leq$ 1.7 ns, and for the UVC transients, 300 fs $\leq \Delta\tau \leq$ 1.7 ns. We note that for the 380 nm transients, the τ_2 lifetimes, attributed to vibrational energy transfer (VET) with the surrounding solvent, are consistently shorter than their 366 nm counterparts suggesting a higher rate of VET. This is likely to be associated with the more vibrationally excited S_0 molecules, which absorb at longer wavelengths and thus are red shifted relative to 366 nm. We note the differences in the lifetimes given compared to those determined by the global fitting procedure, *cf.* Table S1. The reason for this is that global fitting finds the best value for the lifetimes across multiple wavelengths, hence the result is more akin to an average over the spectral region.
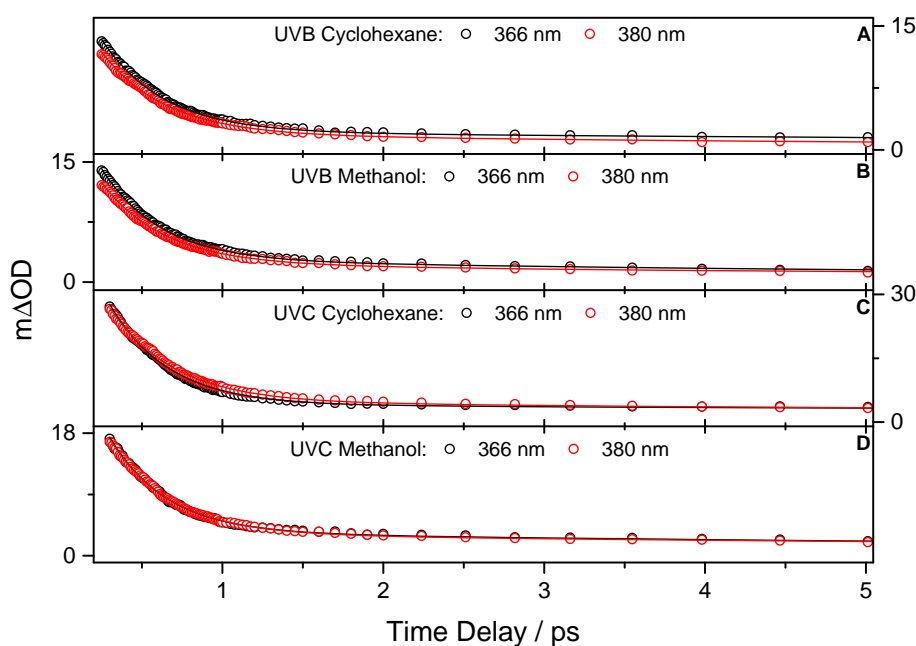

Fig. S8 Raw data are shown as coloured circles; 366 nm transients are shown in black and 380 nm tranisents are shown in red. Transients are fitted with a bi-exponential decay function with lifetimes as summarised in Table S3. OB-cyclohexane and OB-methanol excited with UVB (A) and (B) respectively and OB-cyclohexane and OB-methanol excited with UVC (C) and (D) respectively.

Table S3 Extracted lifetimes for corresponding bi-exponential fits of the raw 366 nm (top table) and 380 nm tranisents (bottom table) as shown in Fig. S8. Here, for succinctness, C=Cyclohexane and M=Methanol. Quoted errors are to 2σ.

366 nm transient:	UVB		UVC	
	C	M	C	M
τ_1 / fs	383 ± 4	366 ± 3	365 ± 5	354 ± 6
τ_2 / ps	11.9 ± 1.3	6.4 ± 0.4	18.5 ± 3.3	8.8 ± 1.0

380 nm transient:	UVB		UVC	
	C	M	C	M
τ_1 / fs	394 ± 7	385 ± 5	396 ± 6	371 ± 5
τ_2 / ps	5.7 ± 0.8	4.8 ± 0.5	9.7 ± 1.3	7.0 ± 0.8

6. Cross correlation signals over the range $355 \leq \lambda \leq 415$ nm

The temporal resolution quoted in the communication of $\sim$100 fs is determined from cross correlation measurements in solvent only scans, methanol being the representative example here. Over the global fitted region of $355 \leq \lambda \leq 415$ nm, the temporal resolution remains consistent, as shown from the cross correlation signals measured at $\lambda = 355$ nm, $\lambda = 385$ nm and $\lambda = 415$ nm, given in Fig. S9. The full width at half maximum (FWHM) returned from a Gaussian fit of the signals is a measure of the temporal resolution at that particular wavelength. As shown in Fig. S9, the resolution is $\sim$100 fs across all wavelengths in the global fitted region.
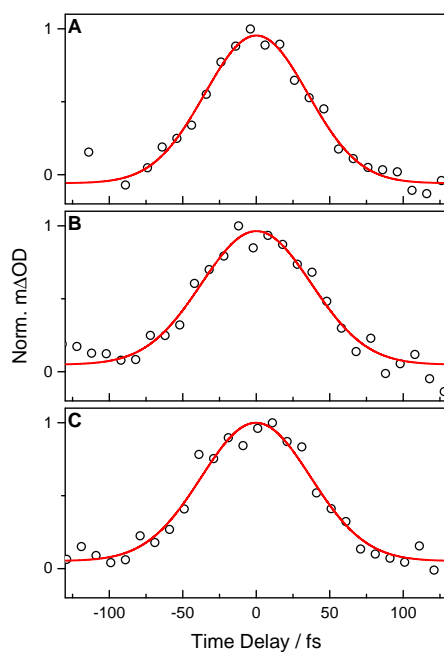
Fig. S9 Cross correlation signals measured in methanol when photoexcited at 243 nm for different wavelengths of the global fitted region of $355 \leq \lambda \leq 415$ nm. (A) For $\lambda = 355$ nm (black circles), the FWHM returned from a Gaussian fit (red line) is 82.5 ± 3.7 fs. (B) For $\lambda = 385$ nm, FWHM $= 88.1 \pm 5.2$ fs. (C) For $\lambda = 415$ nm, FWHM $= 87.7 \pm 4.3$ fs.

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