Ultrafast Photophysical Studies of a Multicomponent Sunscreen: Oxybenzone – Titanium Dioxide Mixtures

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Abstract

Recent studies of the sunscreen constituent oxybenzone have suggested that the dominant mechanism underlying the efficient photoprotection it offers relies on an initial ultrafast enol \(\rightarrow\) keto tautomerisation, followed by nonadiabatic transfer to the ground electronic state. Subsequent collisions with the solvent bath then reform the original enol tautomer.

Utilising femtosecond transient electronic absorption spectroscopy we explore the dissipation of electronic excitation energy in oxybenzone in the presence of titanium dioxide, a widely used, and complementary sunscreen component. We find the relaxation dynamics of this popular organic filter are unaltered by the presence of this favoured inorganic scatterer and the overall dynamics can be described by the additive contribution of the individual constituents. The combination of the two components provides broadband photoprotective properties justifying the widely used organic filter and inorganic scatterer mixtures in commercial sunscreen products.

Keywords: Oxybenzone, Titanium dioxide, Sunscreens, Transient absorption spectroscopy, Ultrafast photochemistry, Solution phase

1. Introduction

Vitamin D is an important biological precursor for various hormones which regulate biochemical tasks \textit{e.g.} calcium absorption. A deficiency in vitamin D has been linked to multiple ailments including rickets and osteoporosis [1, 2]. More than 90\% of metabolised vitamin D in the body is synthesised \textit{via} the ultraviolet-B (UV-B, 315-280 nm) mediated conversion of 7-dehydrocholesterol to previtamin D3 [3, 4]. Thus UV radiation (UVR) and, in particular, UV-B is essential for good health. On the other hand, too much exposure to UVR can have adverse consequences, the most fatal being the development of malignant melanoma [5]. The body is therefore in a delicate balance of the so called \textit{burden of disease}, too much UV exposure and sensitive tissues are damaged, too little and not enough vitamin D is synthesised [6]. The body has evolved to maintain this balance through the development of UV-absorbing melanins distributed throughout the skin that intercept UVR before it reaches these sensitive tissues. The number of melanins and their distribution are regulated through melanogenesis [7], which is up-regulated in environments of high UV exposure or down-regulated in low UV environments in order to maintain an optimal equilibrium in the burden of disease. This however is a delayed process, where any interim response affords little additional photoprotection [8]. An almost universal solution to this has been the development of sunscreens which act to complement natural photoprotection [9–13].

Sunscreens are applied to the upper epidermis of the skin and work by absorbing or scattering harmful UV wavelengths (typically <340 nm) generally through two methods. Organic filters are typically aromatic molecules which absorb UVR and dissipate it through ultrafast pathways. Examples include avobenzone [14, 15], oxybenzone [16–19] and octocrylene [20]. Inorganic scatterers, in addition to absorption, also operate by scattering UV radiation away. Prominent examples include titanium dioxide (\(\text{TiO}_2\)) and zinc oxide [21, 22]. \(\text{TiO}_2\), in particular, is also attracting widespread interest in terms of \(\text{TiO}_2\)-dye photophysics [23, 24]. Most studies of the photoprotection properties of these sunscreen components have focused on individual filters in isolation, but commercial sunscreen products typically contain tens of components in order to produce an efficient, broadband photoprotective and aesthetically pleasing product. In this study we focus on oxybenzone \textit{and} titanium dioxide, two sunscreen constituents which are often combined to provide broad spectral coverage and efficient photoprotection, to understand if the previously observed photodynamics in oxybenzone are changed [16–18] by the presence of the inorganic scatterer. Figure 1 shows the overall relaxation mechanism of oxybenzone. Multi-molecular compositions have already been shown to display photodynamics different to that of the individual constituents, for example, octocrylene is known to behave as a photostabiliser to avobenzone when in solution to-
Photoexcitation populates the $S_1$ state has been previously proposed [16, 17]. (Figure 1: Overall relaxation mechanism of UV photoexcited oxygen couple oxybenzone to the $S_1$ state, hydrogen transfer (ESHT) to the aliphatic C–C bond (iv) couples $S_2$ back to the ground $S_0$ state (v) where vibrational energy transfer (VET) to the surrounding solvent and ground state hydrogen transfer (GSHT) reforms the original enol-tautomer, or (vi) extended rotation can lead to a trans keto-tautomer photoproduction, with an estimated yield of $\sim10\%$ based on transient vibrational absorption measurements [16].)

Figure 1: Overall relaxation mechanism of UV photoexcited oxybenzone as has been previously proposed [16, 17]: (i) Initial UV photoexcitation populates the $S_2(1^1\pi\pi^*)$ state (ii). Excited state hydrogen transfer (ESHT) to the keto-tautomer and internal conversion couple oxybenzone to the $S_1(1^1\pi\pi^*)$ state (iii). Rotation about the aliphatic C–C bond (iv) couples $S_2$ back to the ground $S_0$ state (v) where vibrational energy transfer (VET) to the surrounding solvent and ground state hydrogen transfer (GSHT) reforms the original enol-tautomer, or (vi) extended rotation can lead to a trans keto-tautomer photoproduction, with an estimated yield of $\sim10\%$ based on transient vibrational absorption measurements [16].

made to 50 mL for use in recirculation in TEAS measurements, and were made to 5 mL for all UV-visible measurements. Water was omitted as a solvent due to OBDs poor solubility. Samples are from hereon referred to as: OB-D (10 mM oxybenzone in dioxane), TiO$_2$:OB-D (1 mM TiO$_2$ with 10 mM OB in dioxane), 1 mM-TiO$_2$:OB-M (1 mM TiO$_2$ with 10 mM OB in methanol) and 25 mM-TiO$_2$:OB-M (25 mM TiO$_2$ with 10 mM OB in methanol). All 'steady state' UV-visible spectra are taken with either a Cary 50 or Cary 1E UV-visible spectrophotometer, with a 1 cm path length quartz cuvette (see SI for details), and are shown in Figure 2.

**Pump-probe setup.** The TEAS setup employed in this study is detailed in Reference [28]. Briefly, samples containing OB were photoexcited at 325 nm, while those containing TiO$_2$ only were photoexcited at 330 nm (see UV-visible absorption maxima, Figure 2). The pump pulses have fluences of $\sim1.2 \text{ mJ cm}^{-2}$ and are produced by a commercial optical parametric amplifier (TOPAS-C, Light Conversion) seeded by a 1 kHz pulse train (1 W, 800 nm) from a Ti:sapphire chirp regenerative amplifier (Spitfire Pro XP, Spectra Physics). A small portion of this 800 nm fundamental is used to produce a broadband white light continuum via nonlinear processes in a 1 mm thick CaF$_2$ window, which is used as the probe in the region of $\sim335$–675 nm. A half-wave plate is used to hold the probe polarisation at the magic angle ($54.7^\circ$) relative to the pump polarisation. Samples are recirculated between two CaF$_2$ windows with 100 $\mu$m PTFE spacers via a flow-through cell (Harrick Scientific) from a 50 mL reservoir to ensure a fresh sample for each pump-probe measurement.

**Analysis.** Each recorded transient absorption spectrum (TAS) is first chirp corrected using the KOALA package.

### 2. Experimental Methodology

**Sample preparation.** For all TEAS measurements, samples of oxybenzone (OB, 98%, Sigma-Aldrich), TiO$_2$ nanoparticles (>99%, $\sim21$ nm diameter, P25, Sigma-Aldrich) and the combination of the two, TiO$_2$:OB in dioxane (>99%, Fisher Scientific) or methanol (>99.6%, Sigma-Aldrich), were made. For all solutions containing OB, 10 mM was used. For dispersions containing TiO$_2$, 1 mM and 25 mM (for full saturation) in methanol were used. In dioxane, 1 mM was sufficient for saturation. These ratios were chosen for the extreme ends of what might exist in a commercial product [26]. All samples were made to 50 mL for use in recirculation in TEAS measurements, and were made to 5 mL for all UV-visible measurements. Water was omitted as a solvent due to OBDs poor solubility. Samples are from hereon referred to as: OB-D (10 mM oxybenzone in dioxane), TiO$_2$:OB-D (1 mM TiO$_2$ with 10 mM OB in dioxane), 1 mM-TiO$_2$:OB-M (1 mM TiO$_2$ with 10 mM OB in methanol) and 25 mM-TiO$_2$:OB-M (25 mM TiO$_2$ with 10 mM OB in methanol). All ‘steady state’ UV-visible spectra are taken with either a Cary 50 or Cary 1E UV-visible spectrophotometer, with a 1 cm path length quartz cuvette (see SI for details), and are shown in Figure 2.

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![Figure 2: UV-visible spectra of OB, TiO$_2$ and OB-TiO$_2$ in dioxane (D) and methanol (M). Each spectrum is normalised to its respective maximum.](image-url)
Then a global fitting procedure is used to extract dynamic lifetimes from each TAS [30]. In this global fitting procedure, the experimentally recorded TAS is modelled as the sum of $n$ exponential functions:

$$F(\lambda, \Delta t) = \sum_{i} A_i(\lambda)e^{-\frac{(\Delta t - t_0)}{\tau_i}},$$

where $A_i(\lambda)$ is the decay associated spectrum (DAS) for the $i$th-exponential decay function with lifetime $\tau_i$, and $t_0$ denotes the temporal position of the pump-probe pulse overlap, where the pump-probe time delay is denoted by $\Delta t$. The sum of squares, $F(\lambda, \Delta t)$, of the modelled TAS are minimised with respect to the experimentally measured TAS. For all TAS, $n = 2$, or $n = 3$ if one exponential has a long lifetime. All confidence intervals assigned to lifetimes are reported to the 95% level using support plane analysis [31] (see supplementary information, SI). All global fits include probe spectral regions between 355–415 nm which encompasses the main absorption feature of OB, and begin at a large enough $\Delta t$ so that convolution with an instrument response function is not necessary (see SI). This procedure closely follows that used in previous studies on OB solutions alone [16, 17].

3. Results

Measurements of TiO$_2$ only in methanol (both concentrations) and in dioxane following photoexcitation at the UV-visible absorption maximum (330 nm) are reported in the SI. Minimal dynamics are seen, all of which occur within the temporal resolution of the experimental instrument response function ($\sim$100 fs, [17]), except for when using 25mM-TiO$_2$-M where a strong negative signal is observed which does not fully recover by the maximum available pump-probe delay time of 2 ns. Comparing the spectral location of the negative signal to the UV-visible spectrum of TiO$_2$, this signal can be attributed to a ground state bleach (GSB), which we return to discuss.

TAS for OB-D and TiO$_2$:OB-D following photoexcitation at 325 nm are given in Figure 3. The TAS for OB-D (Figure 3A) shows three features. (i) A negative going signal below 355 nm which, through comparison with the UV-visible spectrum of OB (Figure 2) is assigned to a state bleach (GSB). (ii) An intense positive going signal centred $\sim$365 nm, which decays to the baseline by $\sim$50 ps. (iii) A broad positive signal spanning the probe spectral region $\sim$425–650 nm which decays within $\sim$2 ps. Both positive signals are assigned to excited state absorptions (ESAs) through comparison to previous measurements [16, 17], and ab initio calculations of similar systems [19] which likely originate from transitions to a myriad of electronics states $i.e.$ S$_n \leftrightarrow$ S$_1$. Similar features are observed for the TAS of TiO$_2$:OB-D, with the negative feature (i) appearing more strongly and spectrally broadened. We note that the apparent broadening is consistent with the addition of the TiO$_2$ (most clearly seen for the 25 mM-TiO$_2$ measurements, see SI).

Global fitting is employed in order to quantify the dynamical processes revealed in the TAS. The results of global fitting are summarised in Table 1. Two exponential decay functions were required ($i.e.$ $n = 2$, cf. Eq. 1) to describe the TAS over the probe spectral region of 355–415 nm, which centres on the intense absorption feature (ii). Very early time delays (<300 fs) were omitted to avoid convolution with our instrument response as well.
as a broad feature around time zero (see SI). This analysis reveals two dynamical lifetimes $\tau_1 = 537 \pm 20$ fs and $\tau_2 = 8.3 \pm 3.3$ ps with corresponding DAS shown in Figure 3C, which agree well with previous studies of OB in the non-polar solvent cyclohexane ($\tau_1 = 375 \pm 13$ fs and $\tau_2 = 7.8 \pm 2.8$ ps) [16]. The difference in $\tau_1$ between dioxane measurements and the previously reported cyclohexane and methanol measurements [16] may be understood by the differences in solvent viscosity (vide infra).

The TAS for TiO$_2$:OB-D shown in Figure 3B displays the same features as for OB-D with this addendum. A third lifetime, attributed to the additional negative contribution from the presence of the TiO$_2$ (see SI), was required to describe these TAS. This has the effect of creating a long-lived baseline offset which this third lifetime ($\geq 2$ ns) captures, labelled $\tau_3$. Once again omitting early delay times ($\Delta t < 250$ fs), the other lifetimes are determined to be $\tau_1 = 575 \pm 18$ fs and $\tau_2 = 6.9 \pm 2.8$ ps which correspond very closely to the OB-D measurements.

Next we consider the solvent methanol. Previous measurements determined that OB-M displays two dynamical features, analogous to those discussed for OB-D, with lifetimes $\tau_1 = 368 \pm 13$ fs and $\tau_2 = 4.9 \pm 1.9$ ps [16], and thus provides a point of comparison when TiO$_2$ is included. For low concentrations, 1 mM-TiO$_2$:OB-M, Figure 4A, similar spectral features are seen in the TAS as in the dioxane measurements. Global fitting reveals three dynamical lifetimes, $\tau_1 = 357 \pm 9$ fs, $\tau_2 = 4.8 \pm 1.8$ ps and the long lifetime $\tau_3 \geq 2$ ns. The corresponding DAS are given in Figure 4C. For saturated concentrations, 25 mM-TiO$_2$:OB-M, Figure 4B, the dynamics of TiO$_2$ are much more clearly observed, see SI, whereby the long-time recovery of the GSB persists for the duration of the experiment. Global fitting reveals three lifetimes, $\tau_1 = 363 \pm 11$ fs, $\tau_2 = 3.0 \pm 1.4$ ps and $\tau_3 \geq 2$ ns. For both measurements including TiO$_2$, other than the appearance of the long-lived recovery of the TiO$_2$ which requires the third lifetime, $\tau_1$ and $\tau_2$ compare very closely with OB-M measurements cf. Table 1.

4. Discussion and Conclusions

We can begin to rationalise the features in our measured TAS and assign dynamical processes to the lifetimes determined from global fitting of the TAS by drawing on both $ab$ $initio$ calculations and previous ultrafast measurements [16, 17, 19]. Considering OB-D first, the dynamics observed follow closely those of OB-M and OB-cyclohexane [16]; initial 325 nm photoexcitation populates the $S_2$ state from the ground state, $S_0$. Following this, OB undergoes internal conversion (IC) to the $S_1$ state, followed by an excited state hydrogen transfer (ESHT) along the O–H stretch, forming the $keto$ tautomer. This cascade of processes is captured by the broad absorption feature which is not considered in the global fit, and resides, heavily convoluted, within the instrument response of the experiment of $\sim 100$ fs, which in accord with other $enol$-$keto$ driven
systems [32] and has been confirmed recently via trajectory surface hopping calculations [33]. Rotation about the aliphatic C–C bond is required in order to couple the $S_1$ and $S_0$ states, resulting in a twisted keto geometry and enables population transfer through a conical intersection (CI) between the $S_1$ and $S_0$ potential energy surfaces (PESs), shown in Figure 1. These processes are captured by the lifetime $\tau_1$. This assignment also accounts for the difference in the $\tau_1$ lifetime between solvents, which may be understood through differences in the solvent viscosity, $\eta$. Dioxane exhibits a greater viscosity compared to cyclohexane or methanol ($\eta = 1.19$, 0.897 and 0.551 mPa·s respectively [34]) and is therefore likely to offer greatest friction to the geometry change required before OB can couple to its $S_0$ state [35].

The twisted keto species is not stable on the $S_0$ PES, and there are two routes via which it may relax. (i) The ground state may recover through a reverse tautomerisation involving a ground state hydrogen transfer reforming the enol tautomer, which further relaxes by vibrational energy transfer (VET) to the surrounding solvent molecules. (ii) Formation of a long-lived photoproduct, most likely through extended C–C bond rotation forming a non-chelated, trans keto tautomer as previously reported [16]. However, a possibility remains that the photoproduct might be a phenoxyl radical [18]. The first of these routes appears dominant, given that the majority of the GSB recovers on the time scale of the experiment; the incomplete recovery is therefore attributed to the formation of a photoproduct which does not recover by the maximum time delay available of 2 ns (selected transients are given in the SI). These processes are captured by the lifetime $\tau_2$. This lifetime also displays a solvent dependence; $\tau_2$ is consistently shorter in the more strongly interacting (polar) solvent methanol, which is in agreement with VET driven cooling where a greater degree of hydrogen bonding enhances VET [16, 36]. That being said, it could also indicate that methanol promotes the GSHT but remains convoluted with the VET.

Considering next the TiO$_2$ measurements only, minimal dynamics are observed, the results of which are presented in SI. For low concentrations (1 mM), any dynamics are within the instrument response or are well within the signal to noise of the experiment ($<0.5$ m$\Delta$OD). In methanol, where higher concentrations are achieved (25 mM), there are clear dynamics which persist to the maximum pump-probe time delays. These observations are consistent with previous studies on isolated TiO$_2$ nanoparticles in solution [37–39]. In the low concentration regime, TiO$_2$ displays ultrafast relaxation, likely through the generation and subsequent trapping of surface electrons. At higher concentrations, TiO$_2$ begins to behave more like a thin film, where deep trapping of electrons equilibrating between surface and shallow trapping sites occurs over 100’s of ps [39].

Having characterised the dynamics displayed by each component, individually, we now discuss the measurements for the multicomponent systems. For 1 mM TiO$_2$:OB-D, the TAS (Figure 3B) appears to be a simple weighted sum of the isolated OB and TiO$_2$ systems, with the requirement of the third lifetime accounting for the long-lived dynamics of TiO$_2$. This is further evidenced by similar $\tau_1$ and $\tau_2$ lifetimes for the individual and multicomponent systems (within 2$\sigma$ of each other). Very similar conclusions are reached for both the 1 mM-TiO$_2$:OB-M and 25 mM-TiO$_2$:OB-M systems where all lifetimes are again within 2$\sigma$ of their OB-M counterparts. The effect of the presence of TiO$_2$ in low (or saturated) concentrations on the overall dynamics is simply additive; the presence of one appears not to affect the relaxation dynamics of the other component.

To conclude, the relaxation dynamics of the popular organic filter oxybenzone in commercial sunscreens are unaltered by the presence of the widely utilised scattering (and absorptive) additive TiO$_2$. Unlike other additives such as photostabilisers which are known to enhance the photostability of an organic filter, TiO$_2$ is shown to have minimal impact on the dynamics displayed by the organic filter. This implies, at the very least, very little or no interaction between the two species, e.g., adsorption. This is an important result given the widespread use of TiO$_2$ in commercial sunscreen products and may justify the inclusion of both components in order to provide efficient broadband protection.

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Supporting Information

TiO$_2$ measurements and representative additive spectrum of TiO$_2$ and oxybenzone are given. Global fitting details, residuals from fits, and error analysis are given. Early time transients and selected ground state bleach spectra are presented. Unnormalised UV-visible spectra are presented.

References


