Ultrafast photoprotective properties of the sunscreening agent octocrylene

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Abstract: Today octocrylene is one of the most common molecules included in commercially available sunscreens. It provides broadband photoprotection for the skin from incident UV-A and UV-B radiation of the solar spectrum. In order to understand how octocrylene fulfils its role as a sunscreening agent, femtosecond pump-probe transient electronic UV-visible absorption spectroscopy is utilised to investigate the ultrafast-nonradiative relaxation mechanism of octocrylene in cyclohexane or methanol after UV-B photoexcitation. The data presented clearly shows that UV-B photoexcited octocrylene exhibits ultrafast-nonradiative relaxation mechanisms to repopulate its initial ground state within a few picoseconds, which, at the very least, photophysically justifies its wide spread inclusion in commercial sunscreens.

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References and links
1. Introduction

Ultraviolet-B radiation (UV-B; 280-315 nm) is a minor contribution (~1%) to the daily solar spectrum, being almost completely reflected by the stratospheric ozone layer [1]. The actual % of UV-B reaching the surface of the Earth depends on many environmental variables such as; ozone depletion, cloud cover and solar incidence angle [2,3]. What little of it that does reach the surface of the Earth can impact the biosphere extensively [4,5]. In humans, UV-B mediates the photolytic reaction of 7-dehydrocholesterol to previtamin D$_3$, an early step in the synthesis of Vitamin D [6]. Deleterious effects of UV-B exposure are widely known with photodamage to DNA leading to malignant melanoma being a prominent example. As such, humans have developed extensive photoprotective mechanisms in response to UV-B overexposure. Predominately, UV-absorbing eumelanin is distributed in the skin, the concentration of which can be regulated through melanogenesis in response to varied exposure e.g. tanning of the skin through overexposure [7,8]. However, tanning is a delayed response, after DNA damage could have already occurred. Furthermore, subsequent overexposure to UV-B, even after tanning has taken place, is not always preventative of additional photodamage to the skin [7]. This has led to the wide spread use of sunscreens, which on application to the skin, behaves as a barrier reducing the probability that high energy UV radiation reaches the underlying tissues. Sunscreens therefore work to complement the natural photoprotective mechanisms of the skin.

With respect to this, an effective sunscreen must absorb (or scatter) radiation over a broad spectral range in order to provide protection across all damaging wavelengths of radiation, typically over the ranges of UV-B and the high energy components of UV-A (<340 nm) [9]. As such, sunscreens generally consist of mixtures of organic UV-A and UV-B filters such as cinnamate and benzophenone derivatives, as well as inorganic scattering molecules such as TiO$_2$ and ZnO$_2$ [10,11]. The former are molecules which are photoexcited by radiation and subsequently dissipate their excited state energy via ultrafast (femtosecond (fs) to picosecond (ps) timescales) relaxation pathways, with benzophenones [12–14] and diketones [15] being representative examples.

Octocrylene (OC, see Fig. 1) is one such organic filter whose prevalence is high amongst commercial sunscreens [16]. It displays broadband absorption of UV-B and high energy components of UV-A (<340 nm) [9]. As such, sunscreens generally consist of mixtures of organic UV-A and UV-B filters such as cinnamate and benzophenone derivatives, as well as inorganic scattering molecules such as TiO$_2$ and ZnO$_2$ [10,11]. The former are molecules which are photoexcited by radiation and subsequently dissipate their excited state energy via ultrafast (femtosecond (fs) to picosecond (ps) timescales) relaxation pathways, with benzophenones [12–14] and diketones [15] being representative examples.

Octocrylene (OC, see Fig. 1) is one such organic filter whose prevalence is high amongst commercial sunscreens [16]. It displays broadband absorption of UV-B and high energy components of UV-A radiation, as shown from its UV-visible absorption spectrum in Fig. 1, but has also been shown to act as a stabiliser to other sunscreen constituents, such as avobenzone [17]. In general there remains much ongoing research to understand the potential adverse dermatological (e.g. photoallergies) and physiological effects resulting from the use of sunscreens, including OC [18–20]. OC shows no significant fluorescence or phosphorescence, hinting that ultrafast processes maybe occurring that outcompete spontaneous emission [21]. Closely related molecules, ethylhexylmethoxycrylene and octylmethoxycinnamate have been shown to undergo isomerisation as the dominate relaxation pathway after UV photoexcitation with high efficiency leading to the idea that OC will relax via similar processes [21,22].

In this letter we utilise femtosecond pump-probe transient electronic (UV-visible) absorption spectroscopy (TEAS) to probe the excited state dynamics of OC following photoexcitation at its UV-B absorption maximum ~300 nm (4.13 eV). We determine that OC displays ultrafast relaxation back to its initial ground state after UV-B irradiation, which photophysically, justifies its wide spread inclusion in commercial sunscreens.
Fig. 1. UV-visible spectra of octocrylene (structure shown in inset) in cyclohexane (black line) and in methanol (blue line) displaying a broad absorption peak in the UV-B region centred at ca. 300 nm.

2. Methodology

A stock sample of 97% OC was purchased from Sigma-Aldrich and used without further purification. For all reported TEAS measurements, 10 mM solutions of OC in either cyclohexane (>99%, VWR) or methanol (≥99.6%, Sigma-Aldrich) were recirculated between two CaF$_2$ windows with 100 µm PTFE spacers via a flow-through cell (Harrick Scientific). The samples were photoexcited by 300 nm pump pulses with fluences of ~1–2 mJ cm$^{-2}$ produced by a commercially available 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 the 800 nm fundamental (~5 mW) is focussed into a 1 mm thick CaF$_2$ window producing a broadband white light continuum (~335–675 nm) used as the probe pulses. A half-wave plate is used to hold probe polarisation at the magic angle (54.7°) relative to the pump polarisation. All transient absorption spectra (TAS) are chirp corrected using the KOALA package [23]. Further experimental details may be found in References [24] and [25].

Both the TAS of OC-cyclohexane and OC-methanol were analysed using a global fitting procedure [26, 27]. The experimental TAS are modelled by the sum of $n$ exponential functions convoluted with a Gaussian instrument response function, $G(\Delta t)$:

$$F(\lambda, \Delta t) = \sum_i^n G(\Delta t) \otimes A_i(\lambda) e^{-\frac{(\Delta t - t_0)}{\tau_i}},$$

where $A_i(\lambda)$ is the decay associated spectrum (DAS) for the corresponding exponential decay function with lifetime $\tau_i$, and $t_0$ denotes the temporal position of pump-probe pulse overlap. The sum of squares, $F(\lambda, \Delta t)$, of the modelled TAS are minimised with respect to the experimentally measured TAS. For both OC-cyclohexane and OC-methanol, four exponential functions (i.e. $n = 4$) are required to fully describe the experimental TAS and the $G(\Delta t)$ is taken to be ~100 fs [13]. All confidence intervals assigned to lifetimes are reported to the 95% level using asymptotic standard errors, further details of this assignment methodology can be found in Reference [27].

All ‘static’ UV-visible spectroscopic measurements were taken using a Cary 50 UV-visible spectrophotometer with a 1 cm path length quartz cuvette, and ~µM OC-cyclohexane and OC-methanol solutions. To investigate evidence of long-lived photoproducts, continuous wave
UV irradiation studies were performed on OC using the following procedure. First a static UV-visible spectrum of each sample was taken (Cary 300 spectrometer), to obtain a ‘before’ spectrum. Samples were then irradiated with continuous wave radiation, \(\sim 3\) W, from an arc lamp (OBB, Tunable KiloArc) for 10 minutes using the a central wavelength of 300 nm and bandwidth of \(\sim 20\) nm. A second UV-visible spectrum was taken (Cary 300 spectrometer) following irradiation, referred to as the ‘after’ spectrum. A subtraction of the before spectrum from the after spectrum results in the reported ‘difference spectrum’.

All \(ab\ initio\) electronic structure calculations of OC were performed with the Gaussian 09 computer package [28]. The ground state geometry energy minimum is determined at the DFT/B3LYP/6-311+g** level of theory [29–32]. This minimum was confirmed by normal mode analysis through searches for imaginary frequencies. The presence of imaginary frequencies would otherwise describe a point on the potential energy surface with negative curvature, thus a transition state. The likely excited states were characterised at the TD-DFT/B3LYP/6-311+g** level of theory. Calculations were also performed with the M052X functional for comparison [33].

3. Results

The TAS recorded for OC-cyclohexane and OC-methanol for a range of pump-probe time delays, \(\Delta t\), are shown in Figs. 2(a) and 2(b) respectively. We start by considering the early time (\(\Delta t < 2\) ps) OC-cyclohexane. The TAS are dominated by two positive absorption features: (i) a broad, intense absorption across probe wavelengths \(\sim 335–475\) nm, and (ii) a weaker absorption signal which extends out to, and decays towards the baseline by \(\sim 675\) nm (the limit of our probe spectral window). Both of these positive signals are attributed to the excited state absorption of OC, based on subsequent analysis (\textit{vide infra}). In particular, absorption feature (i) changes significantly for increasing \(\Delta t\), up to 2 ps, see Fig. 2(e). The absorption signal displays an intense peak at \(\Delta t \sim 150\) fs with a short-lived negative signal also observed beyond \(\sim 550\) nm for \(\sim 250 < \Delta t < 500\) fs which we attribute to stimulated emission. As this stimulated emission signal decays, another absorption peak grows in by \(\Delta t \sim 500\) fs, which is most clearly seen at probe wavelengths of \(\lambda \sim 500\) nm, see Fig. 2(a). By 2 ps, the ESA has almost completely returned to the baseline, with no further spectral features observed up to the maximum available pump-probe time delay of \(\Delta t = 600\) ps. Similar features are observed in the TAS of OC-methanol shown in Figs. 2(b) and 2(f).

Table 1. Summary of the Lifetimes of Dynamical Processes of Octocrylene.

<table>
<thead>
<tr>
<th>Lifetime / fs</th>
<th>Cyclohexane</th>
<th>Methanol</th>
</tr>
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<tbody>
<tr>
<td>(\tau_1)</td>
<td>80 (\pm) 10</td>
<td>90 (\pm) 10</td>
</tr>
<tr>
<td>(\tau_2)</td>
<td>120 (\pm) 10</td>
<td>130 (\pm) 10</td>
</tr>
<tr>
<td>(\tau_3)</td>
<td>180 (\pm) 10</td>
<td>200 (\pm) 10</td>
</tr>
<tr>
<td>(\tau_4)</td>
<td>810 (\pm) 140</td>
<td>1520 (\pm) 360*</td>
</tr>
</tbody>
</table>

*Lower limit of unbounded interval used.

Quantitative insight into the dynamical processes observed in the TAS is gleaned from global fitting, where four exponential functions convoluted with a Gaussian instrument response is required to fully describe the TAS. For OC-cyclohexane, global fitting reveals four lifetimes (\(\tau_1, \tau_2, \tau_3\) and \(\tau_4\)) as summarised in Table 1, and are characterised by the corresponding DAS given in Fig. 2(g). The shapes of the DAS are valuable in aiding in the interpretation of the
Fig. 2. (A) Raw TAS of OC-cyclohexane following 300 nm photoexcitation, the colormap indicates the change in optical density (OD), a linear timescale is used up to 2 ps after which a logarithmic scale is used up to 16 ps. (B) Similar observations are seen for 300 nm photoexcited OC-methanol. (C-D) The residuals between the raw TAS and the globally fitted TAS. (E-F) Selected transients at specified wavelengths (see D) highlighting the early delay time changes in the absorption profile for OC-cyclohexane and OC-methanol respectively. Transients have been integrated over a ~5 nm spectral range. (G) The corresponding decay associated spectrum (DAS) for OC-cyclohexane as determined by the global fitting procedure for the four lifetimes described in the main text. (H) DAS for OC-methanol. The amplitude of the DAS for both τ₄ lifetimes has been increased by a factor of five for resolution. Amplitudes are normalised by the amplitude of τ₂.

corresponding TAS. Positive components of the DAS indicate the decay of population from a particular state whereas negative going components indicate a rise in the population of a state. In particular, a negative going component (an exponential rise) concomitant with a positive component (an exponential decay) can be interpreted as a flow of population from the positive region into the negative region, which can be induced by a change in electronic state or by vibrational energy transfer within a single electronic state [34]. The DAS of τ₁, τ₃ and τ₄ are positive indicating a decaying absorption signal whilst τ₂ is negative indicating a growing absorption or stimulated emission feature which agrees qualitatively with the observed absorption features (i) and (ii) of the TAS (Figs. 2(a) and 2(e)). Following an identical procedure, global fitting of the OC-methanol TAS (Fig. 2(b)) reveals four dynamical processes with lifetimes summarised in Table 1 and are characterised by the corresponding DAS given in Fig. 2(h) and display similar features to those discussed for OC-cyclohexane. The confidence interval of the lifetime τ₄ for OC-methanol is unbounded on the positive limit. We suggest this is because of the convolution with an increased photoproduct absorption signal compared to OC-cyclohexane (see Fig. 3), as
such, the lower limit is used (Table 1) [27].

The presence of a ground state bleach (GSB) is not observed which is likely due to the convolution with the strong positive ESA as well as the limit of the probe window being at the tail end of OC’s absorption profile (Fig. 1). Continuous wave irradiation studies were used to investigate any long-lived photoproducts which would typically be signalled by an incomplete GSB recovery. Following the procedure described (vide supra), the resulting difference spectra for OC-cyclohexane and OC-methanol are shown in Fig. 3. There are small discrepancies between the OC-cyclohexane difference spectrum with the corresponding TAS (Fig. 3(a)) whereby the difference spectrum displays a more prominent negative absorption. A similar observation is made for OC-methanol, where a pronounced offset between the difference spectrum and the \( \Delta t = 600 \) ps spectrum around \( \sim 350 \) nm is seen. These features may indicate the presence of a long-lived photoproduct which contributes a minor channel to the relaxation mechanism of OC. Additionally, a broad absorption spans the probe window in both OC-cyclohexane and OC-methanol TAS at \( \Delta t = 600 \) ps. For OC-methanol, there is an emergence of a defined peak centred at \( \sim 375 \) nm. There is no evidence for either of these features in the corresponding difference spectra which suggests that these features may originate from long lived triplet state absorption [17, 21].

Fig. 3. (A) For OC-cyclohexane, continuous wave irradiation results in the difference spectrum (black line) using the procedure described in the main text. Overlaid is a \( \Delta t = 600 \) ps spectrum (blue line). (B) Similarly for OC-methanol. Absorption signals have been normalised with respect to the most negative going signals. (C) Calculated transition energies between triplet states, \( T_n \leftarrow T_1 \). The accessible wavelengths by the probe is highlighted in gray. (D) The output of the KiloArc lamp used for irradiation experiments.
4. Discussion

We now begin to discuss the implications to the photoprotective properties of OC drawing on the different experimental results presented here. We have observed the generation of a photoproduct(s) using continuous wave irradiation, suggesting that there exists a minor relaxation pathway which generates photoproduct(s), suggesting a small probability that OC undergoes photodegradation after UV irradiation, a scenario that has been previously reported [35, 36]. When compared to the TAS of OC for \( \Delta t = 600 \) ps, we observe a weak absorption (\( \sim 100 \mu \text{OD} \)) across the probe window, which is clearly not present in the difference spectrum obtained from continuous wave irradiation measurements. \textit{Ab initio} calculations of triplet-triplet transition energies, as described in the methodology, are shown in Fig. 3(c). These suggest there are a number of triplet states accessible within the probe window (335–675 nm). We therefore suggest this feature can be attributed to triplet state absorption, which is known to be accessible under these conditions, and a property that has been exploited in mixtures with avobenzone to improve its photostability [17, 21, 37]. The spectrum at \( \Delta t = 600 \) ps shows a clear positive peak centred around \( \lambda \sim 375 \) nm for OC-methanol compared to OC-cyclohexane. This might indicate that the rate of intersystem crossing to the triplet state, and/or the absorption cross section between this triplet state and higher lying states increases in the more polar solvent methanol, which may be explained by an increase in solvent perturbations on the excited state energy levels. These observations have an important consequence of OC’s use in sunscreens; the relaxation mechanism of OC only has an apparently minor contribution that involves triplet state absorption or photodegradation, which means there may be a lower probability of OC-containing sunscreens causing adverse dermatological effects, a finding which complements the current literature [16, 35, 36]. Another possibility remains that given the presence of a CN substituent in OC, internal conversion (IC) to a long-lived charge transfer state is another plausible assignment of the photoproduct signal.

Considering next the dynamical processes extracted from the global fitting of the TAS we can attempt to rationalise the dynamics operating in OC after UV-B photoexcitation, although, as we reiterate below, we acknowledge that further work is essential; this discussion however serves as an important starting point. Precedence in the mechanism comes from simple excited state calculations of octocrylene. We found that the likely first excited state, initially populated through excitation by the pump pulse is a \( \pi \pi^* \leftarrow S_0 \) transition, see Table 2 (for molecular orbitals (TD-DFT//B3LYP/6-311+g** shown), transition wavelengths and oscillator strengths) and the static absorption spectra shown in Fig. 1. We also note that both OC-methanol and OC-cyclohexane display similar lifetimes and DAS, suggesting that the proposed dynamics are very similar in both, hence the dynamics discussed are applicable to both systems.

We propose that an initial photoexcitation likely populates an ensemble of close in energy \( n^1 \pi \pi^* \) states \( (n \geq 1) \). The subsequent decay of this population to a lower lying excited state is assigned the lifetime \( \tau_1 \). We suggest this in turn populates another excited \( 1^1 \pi \pi^* \) state with lifetime \( \tau_2 \). We draw confidence with the assignment of \( \tau_1 \) and \( \tau_2 \) by considering the DAS associated with these similar lifetimes (cf. Fig. 2 and Table 1). The positive-going DAS associated with \( \tau_1 \) closely mirrors the negative-going DAS associated with \( \tau_2 \) which might imply a population flow between two states. Furthermore, the negative feature in the TAS assigned to stimulated emission onsets from \( \sim 250 \) fs (see Figs. 2(c) and 2(d)) suggest that it may originate from a state other than the initially populated one(s). Thus \( \tau_2 \) predominately captures the population flowing between these two states by IC, likely \textit{via} a \( n^1 \pi \pi^* \leftarrow m^1 \pi \pi^* \) conical intersection (CI, \( n \neq m \)) given the efficiency this occurs with. We suggest the population on this second state subsequently relaxes with the lifetime of \( \tau_3 \). Since photoexcited OC appears to almost completely recover its ground state, we suggest this state will couple back to the ground state \textit{via} a \( m^1 \pi \pi^* \leftarrow S_0 \) CI and subsequently will relax to the ground vibrational state by vibrational...
energy transfer, likely mediated by a combination of intramolecular vibrational energy redistribution and vibrational energy transfer to the surrounding solvent molecules [38, 39]. This last step is captured by the lifetime \( \tau_4 \), especially the internal conversion to the ground state. An interesting possibility remains in that this relaxation may occur via the isomerisation around the aliphatic C=C, a process suggested to occur in the closely related molecule ethylhexyloxycrylene [21], however, confirmation of this would require further theoretical and experimental studies; for example, one could envisage aromatic ring substitution as one possible technique, but is beyond the scope of this work, and in keeping with the thesis of this work, may trigger further investigations (see below).

There are two important caveats in order here. Firstly, since the lifetimes of the dynamical processes described are similar in magnitude and are very fast, the underlying assumption of the global fitting procedure is that the processes are not sequential begins to break down. This has the effect of clouding the onset of one process with that of another. Ultimately, this means each lifetime will also capture some of the preceding and/or proceeding dynamics, making the absolute assignment of a lifetime with any one process unrealistic [40]. Secondly, there will likely be a contribution to the lifetime(s) (in particular \( \tau_1 \), \( \tau_2 \) and \( \tau_3 \)) from an evolution out of the Franck-Condon window, as well as any solvent rearrangement. These processes typically persist for comparable timescales as the extracted lifetimes, meaning the absolute assignment of population decay from one state to another is highly complex. Furthermore, any spectral shift in the positive absorption signal would likely effect \( \tau_1 \) and \( \tau_2 \). In this case, \( \tau_1 \) and \( \tau_2 \) may describe a spectra shift (on a single potential energy surface), which is consistent with the closely mirrored

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Table 2. First Five Transitions Determined at the TD-DFT//B3LYP(M052X)/6-311+g** Level of Theory.

<table>
<thead>
<tr>
<th>Transition, ( S_n \leftarrow S_0 )</th>
<th>Wavelength / nm</th>
<th>Osc. strength</th>
</tr>
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<tbody>
<tr>
<td>( S_1 \leftarrow S_0 )</td>
<td>336 (295)</td>
<td>0.649 (0.687)</td>
</tr>
<tr>
<td>( S_2 \leftarrow S_0 )</td>
<td>315 (268)</td>
<td>0.657 (0.437)</td>
</tr>
<tr>
<td>( S_3 \leftarrow S_0 )</td>
<td>307 (257)</td>
<td>0.675 (0.477)</td>
</tr>
<tr>
<td>( S_4 \leftarrow S_0 )</td>
<td>298 (251)</td>
<td>0.658 (0.480)</td>
</tr>
<tr>
<td>( S_5 \leftarrow S_0 )</td>
<td>279 (240)</td>
<td>0.643 (0.412)</td>
</tr>
</tbody>
</table>
DAS (Fig. 2(g) and 2(h)). This would mean that the likely relaxation mechanism would be via an nπ*/S₀ CI on the timescale τ₃ followed by vibrational relaxation in the S₀ state captured by τ₄. However, the overall picture of the relaxation dynamics observed in OC is clear; UV-B photoexcited OC undergoes ultrafast non-radiative relaxation which repopulates the ground state with high efficiency. The vast majority of the dynamics are over in the first ~5 ps after photoexcitation, with most of the processes over within the first 2 ps of photoexcitation (Fig. 2). This has major implications for OC’s role as a sunscreens agent since the ability to dissipate energy from UV-B photoexcitation through ultrafast non-radiative processes is vital for a safe and efficient organic filter [17].

Further experimental studies are required to fully understand the states likely to be involved in OC. Specifically, we suggest sequential kinetic studies would provide valuable insight into the observed population flow in both OC-cyclohexane and OC-methanol, a limitation of both our instrument response (~100 fs) and our global fitting procedure [40], which will likely prove useful in the deconvolution of the τ₁, τ₂ and τ₃ lifetimes. Theoretical studies will be invaluable in understanding the states involved in the relaxation mechanism observed in our TAS and indicate if such an isomerisation provides an energetically favourable route to couple back to the ground state. We hope this work will provide a stimulus for further studies along both experimental and theoretical directions.

5. Conclusion

In summary we have provided initial ultrafast measurements of the commonly used sunscreen molecule octocrylene, which is shown to exhibit an ultrafast relaxation mechanism predominantly via nonradiative pathways, with high efficiency. Furthermore, non-polar and polar solvents show little effect on the predominate dynamics, but with some noticeable effects on potential triplet state formation. These measurements highlight the efficiency of octocrylene as used as a sunscreen molecule and suggest there is minimal triplet state absorption and photodegradation, important properties for sunscreens.

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