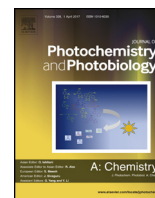




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Photophysics of the sunscreen ingredient menthyl anthranilate and its precursor methyl anthranilate: A bottom-up approach to photoprotection



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ABSTRACT

The ultrafast excited state dynamics of the sunscreen ingredient menthyl anthranilate (MenA) and its precursor methyl anthranilate (MA) were studied in vacuum (using time-resolved ion yield spectroscopy) and in solution (using transient electronic absorption spectroscopy). MenA and MA both show long-lived dynamics, with the observation of a kinetic isotope effect suggesting that hydrogen motion acts as the rate determining process in the overall decay. Complementary computational studies exploring the intuitive decay pathways of MA revealed a bound S_1 state with a shallow 'up-hill' gradient with respect to proton transfer. From these results, it is suggested that photoexcited population is trapped in this excited state from which luminescence occurs as a prominent decay pathway. This work has shown that the photophysics of MA and MenA – and hence their photoprotection capabilities – are not drastically influenced by aliphatic structure or solvent environment alone. A *bottom-up approach*, such as the one described herein, is essential to understand the combination of factors that afford optimum photoprotection and to develop a new generation of tailor made, efficacious sunscreens.

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1. Introduction

The damaging effects of excessive exposure to ultraviolet (UV) radiation to living organisms are well documented in the literature [1–3]. Such damages include erythema [4], a result of excessive skin irradiation with UV-A (400–315 nm) and/or UV-B (315–280 nm) radiation – both of which are directly absorbed by several chromophores in human skin (e.g. melanins, acids and kynurenines). UV-A radiation is also linked to production of free radicals and skin aging [5], whilst UV-B radiation can be directly absorbed by DNA and initiate the photochemistry responsible for mutagenic photolesions (e.g. cyclobutane pyrimidine dimers) [6]. If repair mechanisms fail to correct these photolesions in DNA, this damage may result in carcinogenesis [7]. While the human skin has its own natural photoprotection mechanisms (provided by melanin pigments), these are often insufficient for continued and excessive sun

exposure. Photoprotection products, such as sunscreen lotions, are therefore required in order to provide enhanced protection against UV-induced damage. Since their appearance in the early 20th century [8], sunscreen usage has evolved from simply providing protection against sunburn to being perceived as primary prophylaxis, actively preventing skin aging and skin cancer [9]. Despite attempts to raise awareness of the risks associated with excessive sun exposure and the widespread availability of sunscreen lotions, the incidence of skin cancer has increased in recent years [10]. There is, therefore, an obvious urgency for more effective sunscreens.

An ideal sunscreen molecule should absorb across (and hence provide protection against) the UV-A and UV-B wavelength range of the solar spectrum [11]. One would expect sunscreen molecules to also have the ability to dissipate the absorbed excess energy rapidly – on an ultrafast timescale, i.e. femtosecond (10^{-15} s) to picosecond (10^{-12} s) – without detriment to molecular structure. Such detrimental photochemistry may be both intramolecular (fragmentation, isomerisation, etc.) and/or intermolecular (chemical reactions with other species in the sunscreen mixture or in the

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skin itself) [12–15]. The study of the photodynamics that follow the absorption of UV radiation (photoexcitation) of sunscreen molecules has only recently gained momentum [14–21] and therefore these mechanisms remain poorly understood.

While reports on the ultrafast photodynamics of commonly used sunscreen molecules, such as cinnamates and sinapates [16–18,20], already exist, analogous information is not available for anthranilates such as methyl and menthyl anthranilate (MA and MenA, Fig. 1). MA is a food grade flavour and fragrance additive used in personal care products [22] and is also a precursor to MenA (commercial name *Meradimate*), a sunscreen component approved by the US Food and Drug Administration [23]. In general, the anthranilates are considered to be a photostable (non-degradable upon exposure to UV) class of sunscreens due to the intramolecular hydrogen bonding facilitated by the *ortho* position of the NH₂ group with respect to the ester substituent [24]. Interestingly, however, under anaerobic conditions, a photodegradation mechanism was found to occur for MA upon UV exposure [25]. Under aerobic (more realistic) conditions, an appreciable quantum yield of fluorescence (~ 0.376 – 0.549) was observed in various solvents [26], as well as a 280 μ s triplet state lifetime in aqueous solution [22]. Smaller quantum yields for singlet oxygen sensitisation have also been reported for MA [22]. Such radiative and non-radiative processes persist in MenA, which presents large quantum yields for fluorescence (0.64 ± 0.06 in ethanol) [23] and intersystem crossing (0.34 in ethanol at room temperature) [27]. The presence of triplet states in solvated MenA was confirmed by Kikuchi et al. [27] by using a triplet quencher; the lifetime of the triplet state was determined to be 2.36 s [27].

In light of the available literature, it seems that photoexcited MA and MenA dissipate excess energy *via* radiative decay, which is perceptibly not ideal in a sunscreen molecule [14]. The radiative decay observed in MA and MenA is at odds with other sunscreen molecules which tend to decay to their ground electronic states *via* non-radiative internal conversion (IC) on an ultrafast timescale [16,19]. It is now well understood that ultrafast IC between electronic states is facilitated by conical intersections (CIs) which arise when certain nuclear motions (*e.g.* isomerisation and bond-stretches) drive distinct electronic states towards degeneracies in configuration space [28]. In related sunscreen molecules, many CI geometries – ranging from *trans-cis* isomerisation to ring deformations, for example – have been identified as likely contributors driving ultrafast IC from the excited to ground state

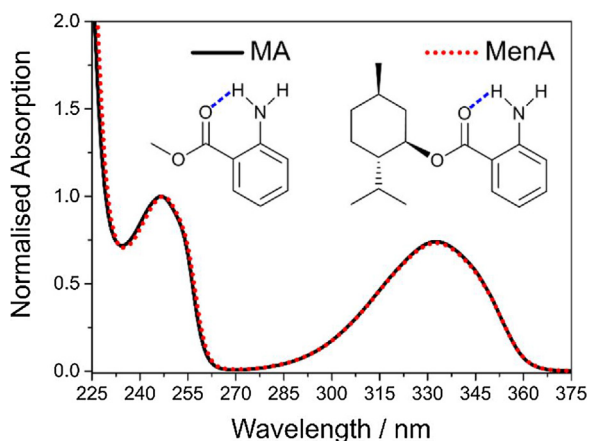


Fig. 1. UV/Visible absorption spectrum of methyl anthranilate (MA, black solid line) and menthyl anthranilate (MenA, red dotted line) in cyclohexane. The molecular structures of each molecule are also shown, with the intramolecular hydrogen bond indicated with a blue dashed line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[16,17,29]. For some sunscreen molecules, notably oxybenzone, isomerisation is preceded by an *enol-keto* type hydrogen atom motion; *keto* oxybenzone then isomerises back to ground state *enol* oxybenzone [19]. Such tautomerisation processes typically occur on ultrafast timescales, *i.e.* on much shorter timescales than those probed in the aforementioned MA and MenA studies.

The non-unity luminescence quantum yield of MenA suggests other, non-radiative, photophysical processes are also involved in its relaxation mechanisms. Ultrafast spectroscopy techniques were employed in the present work to identify these ultrafast photophysics taking place in photoexcited MenA and hence further inform on its suitability as a sunscreen ingredient. In keeping with a *bottom-up approach*, by which the effects of increasing molecular complexity are evaluated [14], both MA and MenA were studied. Moreover, spectroscopic techniques were employed both in vacuum and in solution to evaluate the environmental effects on the intrinsic photodynamics of these molecules. Computational studies were also performed to complement the experimental measurements and provide further detail on the topography of the electronic states of the molecules studied. This work highlights the importance of investigative studies targeting the intrinsic molecular and electronic characteristics that provide sunscreen molecules with their photoprotection capabilities.

2. Experimental methods

2.1. Absorption spectra

The UV/Visible absorption spectra of MA (Alfa Aesar, 99%) and MenA (Aldrich, 98%), shown in Fig. 1, were obtained using a PerkinElmer Lambda 850 UV/Vis spectrophotometer. The sample of each molecule was prepared by dissolving MA or MenA in cyclohexane (99%, Fisher Scientific) with a concentration of approximately 10^{-6} M.

2.2. Time-resolved ion yield (TR-IY)

The time-resolved ion yield (TR-IY) set up used in this work has been described previously [30–32] and is therefore only briefly described here, with further details of particular experimental conditions provided where necessary. A commercial femtosecond (fs) Ti:Sapphire oscillator (Spectra-Physics Tsunami) and regenerative amplifier (Spectra-Physics Spitfire XP) were used to produce ~ 40 fs laser pulses of ~ 3 mJ per pulse centred at 800 nm. The fundamental 800 nm output was subsequently split into three beams, each with ~ 1 mJ per pulse. One of these beams was used to pump an optical parametric amplifier (Light Conversion, TOPAS-C) to generate “pump” (λ_{pu}) pulses centred either at 300 nm (4.13 eV), 315 nm (3.94 eV), or 330 nm (3.76 eV). These wavelengths were chosen to sample the UV-A and UV-B regions of the solar spectrum and the broad absorption feature shown in Fig. 1 while maintaining adequate signal to noise ratios. A second laser beam pumped a separate TOPAS-C which was used to generate 260 nm “probe” (λ_{pr}) pulses. The pump and probe pulses were temporally delayed with respect to each other (with a delay time of Δt) by reflecting the pump off a hollow corner gold retroreflector mounted on a motorised delay stage allowing a maximum temporal delay of 1.2 ns.

The two laser beams intersected a molecular beam which was produced by seeding the target molecules, heated to 50 °C (MA) or 90 °C (MenA), into helium (~ 3 bar). The gaseous mixture was then expanded into vacuum ($\sim 10^{-7}$ mbar) using an Even-Lavie pulsed solenoid valve [33]. At the point of intersection, λ_{pu} excited the species in the molecular beam and λ_{pr} ionised any excited (or photodissociated) species. The resulting ions were focused onto a detector, consisting of two microchannel plates (MCPs) coupled to

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