

Photocleavage of Coumarin Dimers Studied by Femtosecond UV Transient Absorption Spectroscopy

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Ultraviolet (UV) light is a potent element in the photodecomposition of molecular systems. It is generally detrimental, with a classic example being the cyclobutane ring formation in DNA between thymine nucleobases, which leads to mutagenic DNA lesions.^[1] It is also known that by exposure to other frequencies of UV or visible light some UV-induced photoreactions can be reversed.^[2] Such controlled selectivity is a highly desirable feature for enhancing the capabilities of synthetic chemistry. Unfortunately, whilst various examples of photoinitiated ring opening and closing are known, the mechanisms behind these processes remain under debate. Coumarins are a known class of synthetic chromophores that display wavelength-tunable ring opening and closing behaviour.^[3] Quantum yields of formation and have found to differ in coumarin units of different stereoisomer structure and chemical substituent content.^[4-6]

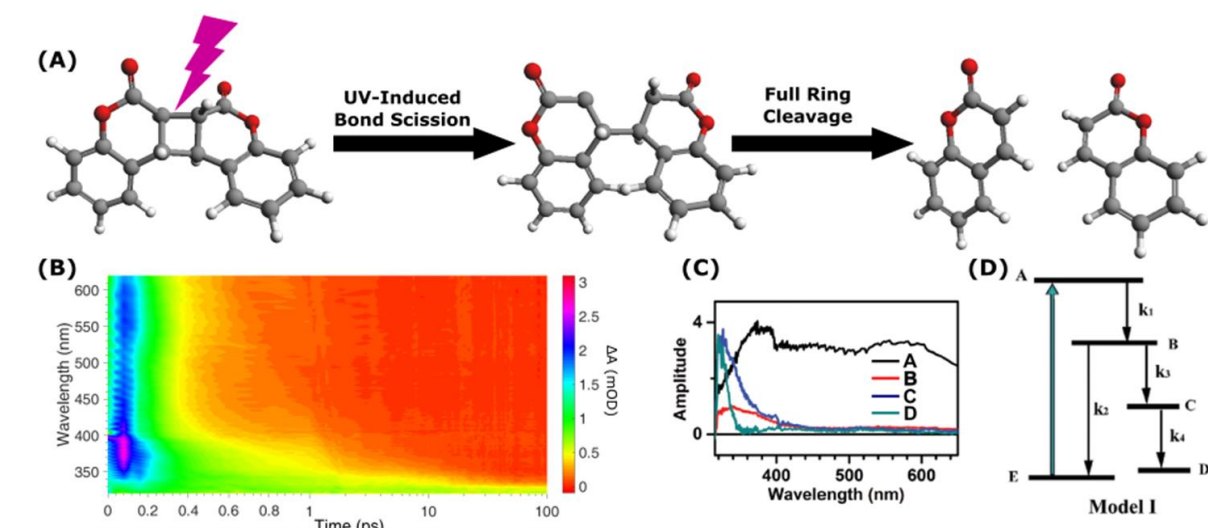


Figure 1: (A) Schematic of the coumarin dimer cleavage mechanism proceeding via a stepwise bond scission mechanism. Purple arrow represents exposure to UV photons at <280 nm. (B) Surface map of the transient absorption data acquired for *anti*-hh dimers. (C) Species associated spectra (SAS) extracted from the transient absorption data using a 4 excited state species, global analysis model. (D) Schematic of the global analysis model found to best fit the experimental data. Ground state dimer is labelled as E, and all excited states species are labelled in accordance with the SAS spectra in Fig. 1C.

In an effort to bring further understanding to the properties behind such photochemical reactions, we studied unsubstituted coumarin dimers in three isomer forms: *anti*-hh, *syn*-hh and *syn*-ht. The isomers were studied using femtosecond UV pump, visible probe transient absorption spectroscopy.^[7] UV pump pulses, with sub-30 fs pulse duration and resonant to the lowest optical transition of the coumarin dimers, was used to trigger the photocleavage (Fig. 1A). The dynamics were tracked up to 100's of picoseconds, with a probe range of 320-660 nm (Fig. 1B), enabling us to monitor the stages of the dimer excited state, progression of the ring opening, and the formation and relaxation of the coumarin monomer products.

Analysis of the transient absorption data, with respect to previous two-photon absorption studies,^[8,9] plus recent transient electronic^[10] and vibrational^[11] absorption spectroscopy of coumarin monomers, revealed the dimer ring opening to be a sequential, stepwise bond scission process (Fig. 1A). Formation of the intermediate state, and subsequent loss of the initial dimer excited state, occurs within 200 fs. The quantum yield was found to be modulated by the steric repulsions and radical intermediate stabilisation, which are in turn dependent on the stereochemistry of the coumarin dimer in question. The data revealed that, under the UV excitation conditions used, the mechanism is not related to the classical, pericyclic descriptions surrounding [2+2] cycloadditions. Global analysis of the data also allowed us to build a simple model that can characterise the main stages of the photocleavage (Fig. 1C-D).

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