

Supporting Information

Towards Elucidating the Photochemistry of the Sunscreen Filter Ethyl Ferulate Using Time-Resolved Gas-Phase Spectroscopy

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A. UV/Vis Spectrum of ethyl ferulate (EF) in cyclohexane

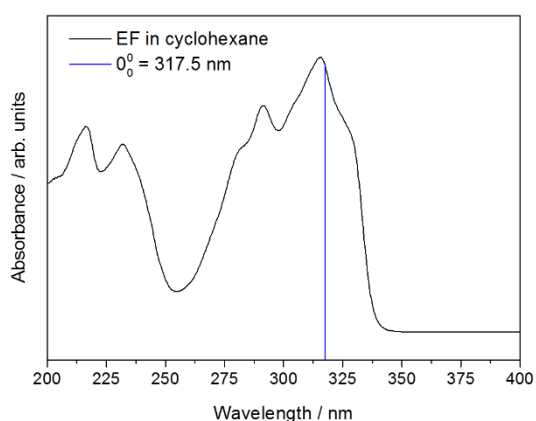


Figure S1. Ultraviolet/Visible (UV/Vis) absorption spectrum of EF in cyclohexane. The blue line represents the molecule's origin band (S_1 ($v = 0$)) in the gas phase at 317.5 nm. Thermal fragmentation and the presence of several conformers of EF complicates the vapour phase UV/Vis spectrum of EF, hence the choice of cyclohexane as a solvent.

B. Kinetic Fits

TR-IY transients, $f(\Delta t)$, are modelled using a sum of exponential decays, both in positive (forward dynamics) and negative (reverse, or probe-pump, dynamics) time, convoluted with a Gaussian instrument response function (IRF), $g(\Delta t)$, which was measured to be approximately 140-160 fs:

$$f(\Delta t) = g(\Delta t) \otimes \sum_{n,m} \left(A_n e^{\left(\frac{-(t-t_0)}{\tau_n} \right)} \right) + \left(B_m e^{\left(\frac{-(-t+t_0)}{\tau_m} \right)} \right)$$

In the equation above, A_n corresponds to the amplitude of each exponential decay function describing the forward dynamics and τ_n represents the associated time constant; B_m corresponds to the amplitude of each exponential decay function describing the reverse dynamics and τ_m represents the associated time constant.

In the fits for MVP and ConA, one forward and one reverse component were necessary for a good fit. For the EF fits, while there are no reverse dynamics to model, three exponential decays are needed to successfully fit the data.

C. Trial exponential decay fits for EF

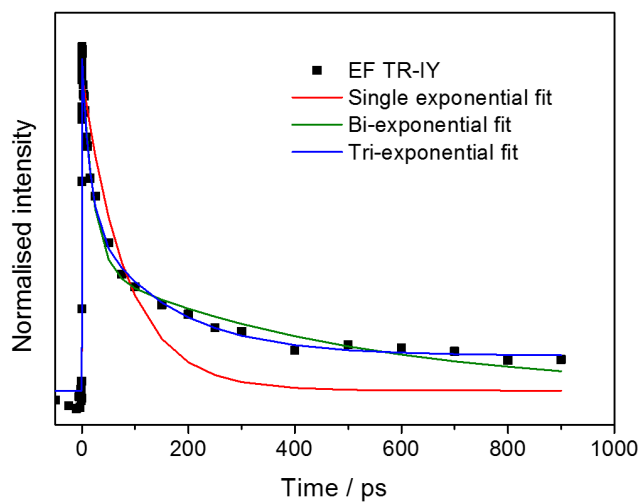


Figure S2. Attempted kinetic fits for the TR-IY data in EF with one (red), two (green) and three (blue) exponential decays. These kinetic fits were calculated using the same methodology as detailed in Section B above. The bi-exponential fit clearly breaks down at long times, whereas the tri-exponential fit is excellent at all delay times.

D. Total Kinetic Energy Release (TKER) spectra for MVP and ConA

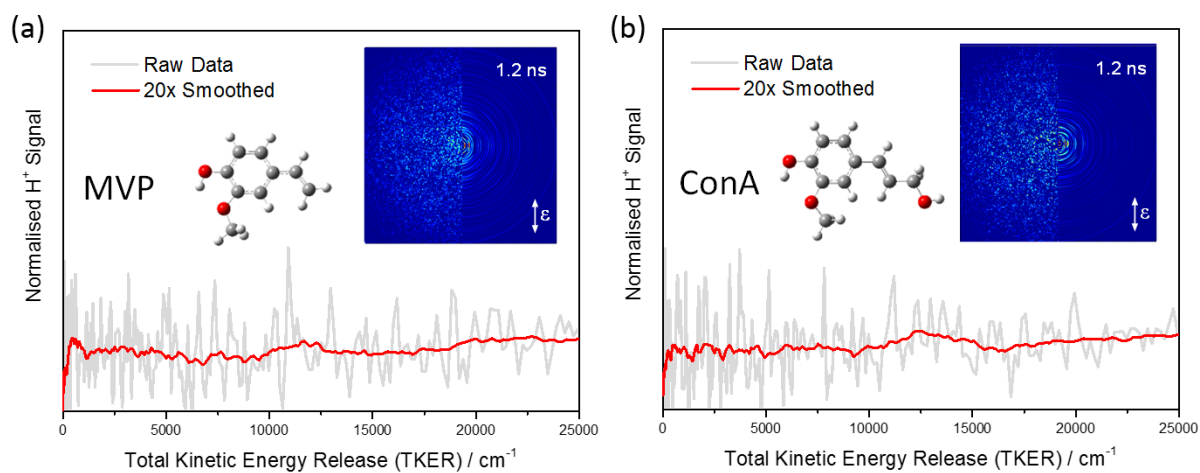


Figure S3. TKER spectra for (a) MVP excited at 305 nm and (b) ConA excited at 306 nm, probed at 243 nm. Both spectra are featureless, suggesting that O–H bond fission mediated by $\pi\sigma^*$ states is not a viable pathway for either of these molecules within the 1.2 ns timescale that can be probed with this experiment.

E. Off resonance TKER spectrum for EF

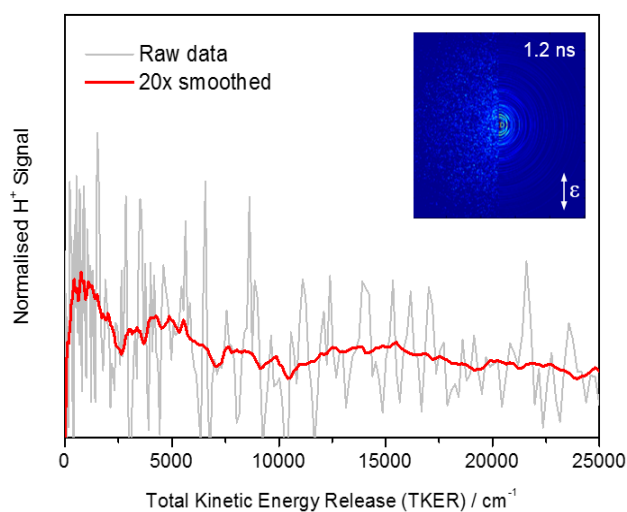


Figure S4. TKER spectrum for EF off resonance with the $2s \leftarrow 1s$ transition in atomic hydrogen (245 nm) exciting at 317.5 nm. There is still evidence of the low energy Boltzmann-like feature, suggesting this is from multiphoton dissociative ionisation processes.

F. Time-of-flight mass spectrum for EF at 317.5 nm pump and 200 nm probe

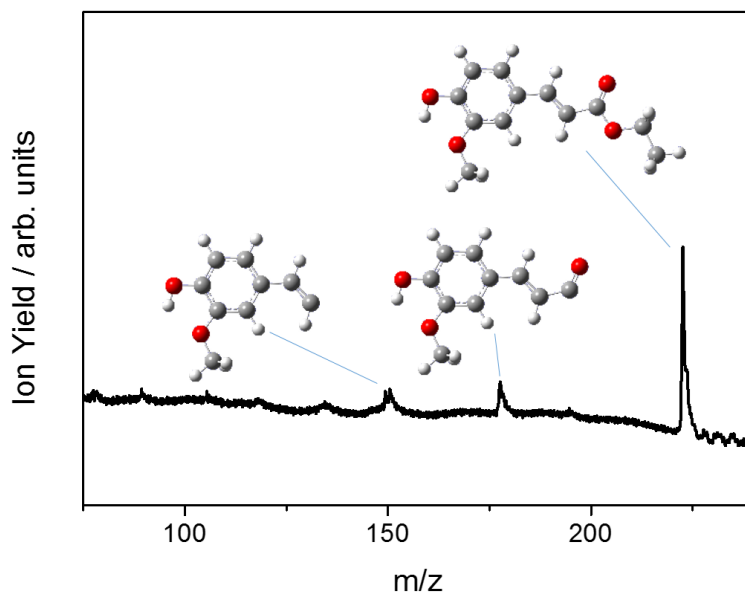


Figure S5. Time-of-flight mass spectrum of EF showing fragmentation of the side chain of the molecule into various fragments.

G. CAM-B3LYP/cc-pVDZ triplet state calculations of EF

Table TS1. Singlet and triplet state vertical excitation energies of EF calculated using Gaussian09 at the CAM-B3LYP/cc-pVDZ level of theory in the region of interest (around the S_1 vertical excitation energy).

Type of State	Energy / cm^{-1}
$1^1n\pi^*$ (S_2)	39118
$1^1\pi\pi^*$ (S_1)	34843
$^3n\pi^*$	34221
$^3\pi\pi^*$	34082
$^3\pi\pi^*$	32147
$^3n\pi^*$	26883

H. EF fluorescence lifetimes

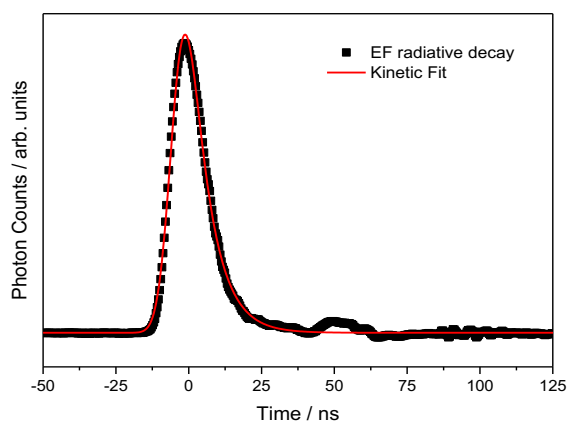


Figure S6. Total fluorescence lifetime measurement for EF upon photoexcitation at 317.55 nm. The lifetime for radiative decay extracted from this measurement is 6.9 ± 0.1 ns. The instrument response is 9.2 ± 0.1 ns. This fit follows the same method explained in B.