Electronic Supplementary Information for:

'Probing ultrafast dynamics in photoexcited pyrrole: timescales for $^1\pi\sigma^*$ mediated H-atom elimination'

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Figures: S1 – S3

S1. Fitting methods

a. Kinetic modelling of the H^+/D^+ signal transients

H^+/D^+ signal transients obtained from either time-resolved ion yield (TR-IY) or time-resolved velocity map ion imaging (TR-VMI) measurements are modelled using a combination of exponential rise and decay functions, which are convoluted with the Gaussian instrument response function, $g(\Delta t)$.

At 250 nm we use a combination of: (*i*) an exponential rise, $f(\Delta t)$, which describes the rapid rise in signal at $\Delta t > 0$ attributed to probed H/D-atoms generated through rapid N-H/D bond fission along the state; (*ii*) an exponential decay, $d(\Delta t)$, which accounts for the sharp 'spike' in signal around $\Delta t = 0$; and (*iii*) a second exponential rise function at $\Delta t < 0$, $r(\Delta t)$, which models the 'reverse dynamics' observed at 250 nm. These functions are each convoluted with the Gaussian instrument response function, $g(\Delta t)$, and have the forms:

$$\begin{aligned} f(\Delta t) &= g(\Delta t) * \left[1 - A\exp\left(-\frac{\Delta t}{\tau_f}\right)\right] \\ d(\Delta t) &= g(\Delta t) * \left[B\exp\left(-\frac{\Delta t}{\tau_d}\right)\right] \\ r(\Delta t) &= g(\Delta t) * \left[1 - C\exp\left(\frac{\Delta t}{\tau_r}\right)\right] \end{aligned} \quad , \tag{S1}$$

where *A*, *B* and *C* are the amplitudes of each function, τ_f, τ_d and τ_r are the time-constants associated with each exponential function and Δt is the pump-probe time delay. The overall fit equation at 250 nm, $a_{250nm}(\Delta t)$, is subsequently given as

$$a_{250nm}(\Delta t) = f(\Delta t) + d(\Delta t) + r(\Delta t). \tag{S2}$$

We note that the D^+ signal transient obtained from photolysis of pyrrole-d_1 at 250 nm (Fig. 4(b), main discussion article), was fitted only to data recorded at $\Delta t \geq 1$ ps using only the $f(\Delta t)$ function in eqn (S1). Due to the very low D^+ signal levels and reduced 'shot-to-shot' noise observed in these experiments, it was not possible to perform a reliable 243.1 nm one-colour background subtraction (unlike the H^+ transient from undeuterated pyrrole at 250 nm). Given that the location of $\Delta t = 0$ is known (see section 2 of main article), fitting signal only associated with the 'forward' rise (after $\Delta t \geq$ 1 ps) therefore enables an estimate of the 'baseline' signal level (*i.e.* zero two-colour D^+ signal), as indicated by the 'normalised' D^+ signal scale in Fig. 4(b) of the main article.

At 238 nm, fitting of the H^+/D^+ transients only requires 'forward' and 'reverse' dynamics and subsequently, the overall fit is given by:

$$a_{238nm}(\Delta t) = f(\Delta t) + r(\Delta t). \tag{S3}$$

Finally, the 'high TKER' and 'low TKER' H^+ signal transients recorded at 200 nm (see main article for details) are fitted using:

$$\begin{aligned} a_{200nm}^{high}(\Delta t) &= f(\Delta t) \\ a_{200nm}^{low}(\Delta t) &= f_L(\Delta t) + f_{stat}(\Delta t) \end{aligned} \quad , \tag{S4}$$

Where $a_{200\text{nm}}^{\text{high}}(\Delta t)$ and $a_{200\text{nm}}^{\text{low}}(\Delta t)$ are the overall fit functions for the high TKER and low TKER signal transients, respectively. In the function $a_{200\text{nm}}^{\text{low}}(\Delta t)$, two individual exponential rise functions, $f_{\text{L}}(\Delta t)$ and $f_{\text{stat}}(\Delta t)$, are required to model the bi-exponential rise profile of the recorded transient, each with associated time-constants of τ_{L} and τ_{stat}, respectively.

b. TKER spectrum fit at 200 nm

The TKER spectrum recorded at 200 nm after Δt = 1.2 ns, presented in Figs. 6(a) of the main manuscript (and Fig. S3) is fitted to the sum a 'statistical' function and an extreme value (Gumbel) distribution, to indentify the degree of 'overlap' between the low TKER signal component (modelled by the statistical function) and the high TKER signal component (modelled by the Gumbel function) between 5000 – 10000 cm^{-1}. The overall fit, $I(x)$, has the functionality:

$$I(x) = I_0 + \left[\frac{A\sqrt{x}}{\exp(x/\rho)}\right] + \left[B\exp\left(-\frac{(x-\mu)}{\sigma}\right)\exp\left\{-\exp\left(-\frac{(x-\mu)}{\sigma}\right)\right\}\right] \qquad \text{(S5)}$$

where x is the TKER, I_0 is the baseline signal level, A is the amplitude of the statistical function, ρ is the statistical function width, B is the Gumbel function amplitude, μ is the location parameter of Gumbel distribution, and σ is the width parameter of Gumbel function.

S2. β_2 recoil anisotropy parameters at 238 and 200 nm

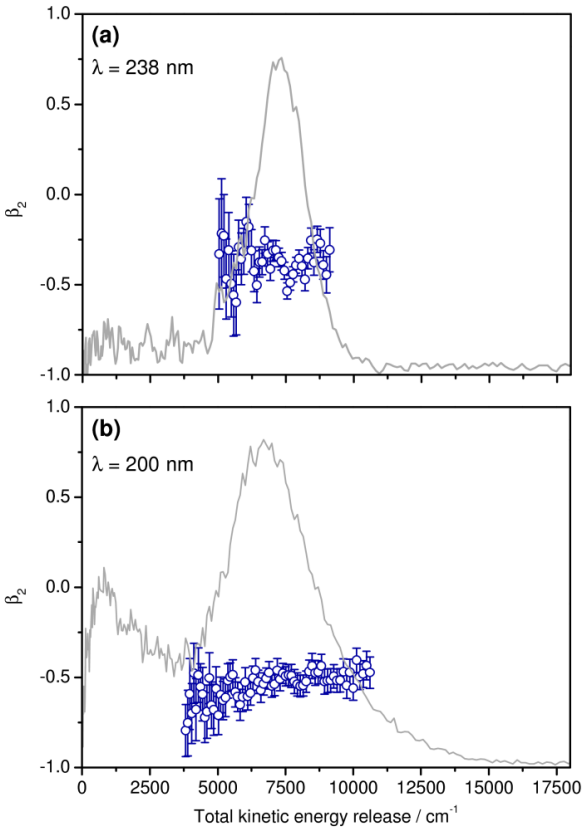

Fig. S1 β_2 recoil anisotropy parameters as a function of TKER at Δt = 1.2 ns after excitation at (a) 238 nm and (b) 200 nm.

S3. D^+ signal transient at 238 nm

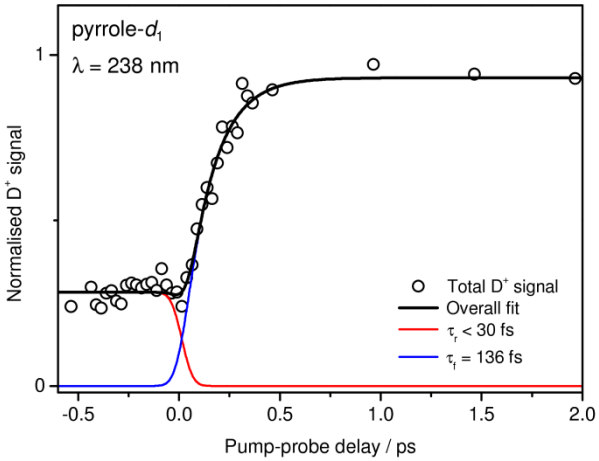

Fig. S2 Normalised D^+ signal transient from pyrrole-d_1 obtained using TR-IY (open circles), with a 238 nm pump and 243.1 nm probe combination, together with the resultant kinetic fit (black line). A one-colour 243.1 nm background signal has been subtracted from the displayed transient. Individual fit components associated with τ_f = 136 fs (blue) and τ_r < 30 fs (red) are also shown.

S4. TKER spectrum fit at 200 nm (Δt = 1.2 ns)

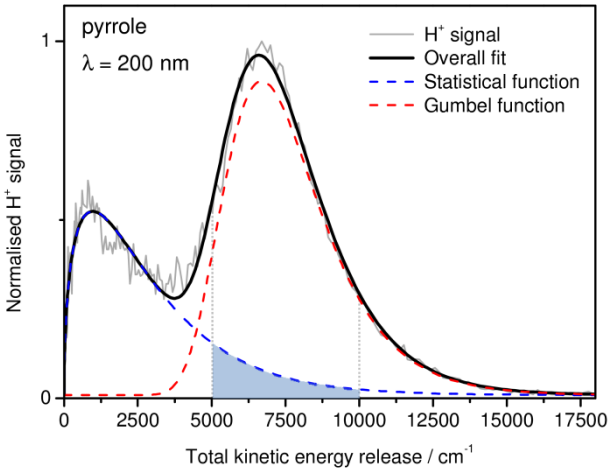

Fig. S3 TKER spectrum (grey) recorded following photolysis of pyrrole at 200 nm with a pump-probe time delay of Δt = 1.2 ns. An overall fit to the TKER spectrum using eqn (S5) is shown by the solid black line. The 'statistical' and Gumbel function components of the overall fit are shown by the dashed blue and red lines, respectively. The blue shaded region indicates the ~7% of 'low TKER' signal which contributes to the total observed signal between 5000 – 10000 cm^{-1} – see ref. 59 in the main article for further details.