Electronic Supplementary Information for:
‘Manipulating dynamics with chemical structure: Probing vibrationally-enhanced dynamics in photoexcited catechol’

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Figures: Figs. S1 – S10

S1. Kinetic analysis of the H$^+$ and catechol$^+$ signal transients

Ion 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, \( g(\Delta t) \).

All catechol$^+$, guaiacol$^+$ and [catechol-$d_2$]$^+$ parent signal transients are fitted to a bi-exponential decay function, \( P(\Delta t) \), which has the functionality:

\[
P(\Delta t) = \left[ g(\Delta t) \ast A \exp \left( -\frac{\Delta t}{\tau_d} \right) \right] + \left[ g(\Delta t) \ast B \exp \left( -\frac{\Delta t}{\tau_f} \right) \right].
\]  

(S1)

H$^+$ and D$^+$ signal transients extracted \textit{via} integration over the range 5000 – 8000 cm$^{-1}$ in TKER spectra (between 280.5 – 254 nm), where tunnelling dynamics are active (see Fig. S5), are fitted to a bi-exponential rise function, \( H_\gamma(\Delta t) \):
Across the range 250 – 243 nm, H+ signal transients (over 5000 – 8000 cm⁻¹) display a ‘spike’ in H+ signal at Δt = 0 which then rapidly decays within the instrument response (~120 fs). This feature is a result of undesired multiphoton processes, which generate and ionise neutral H-atoms at the temporal overlap of both the pump and probe pulses, and increases in amplitude as the pump wavelength is tuned closer to 243 nm (see Fig. S5). To account for this, these transients are fitted using a modified version of eqn (S2), $H_T(Δt)$, which contains an additional exponential decay function:

$$H_T(Δt) = \left[ g(Δt) * \left( 1 - A \exp\left( \frac{-Δt}{τ_f} \right) \right) \right] + \left[ g(Δt) * \left( 1 - B \exp\left( \frac{-Δt}{τ_f} \right) \right) \right] + \left[ g(Δt) * C \exp\left( \frac{-Δt}{τ_m} \right) \right]. \quad (S3)$$

Finally, H+ signal transients generated via integration over the range 10000 – 14000 cm⁻¹, between 254 – 237 nm (Fig. S6), are fitted using an exponential rise and decay function, $H_{CI}(Δt)$:

$$H_{CI}(Δt) = \left[ g(Δt) * \left( 1 - A \exp\left( -\frac{Δt}{τ_{CI}} \right) \right) \right] + \left[ g(Δt) * B \exp\left( -\frac{Δt}{τ_m} \right) \right]. \quad (S4)$$

**S2. Orbital hypersurfaces**

![Fig. S1 Hypersurfaces of orbitals used in CASPT2 and CASSCF calculations. All presented orbitals are used in the (12,10) active space for CASPT2 calculations, while the three π, two n, and three π* orbitals are used in a reduced (10,8) active space for CASSCF calculations of the S1_min structure.](image)
S3. Power dependence studies at \( S_1(v = 0) \): \( \lambda = 280.5 \) nm

![Graph showing power dependence studies](image)

**Fig. S2** Catechol\(^+\) parent ion signal transients (grey diamonds) obtained following excitation at 280.5 nm with pump pulse energies of (a) 4.5 \( \mu \)J/pulse and (b) 60 nJ/pulse. Overall kinetic fits using eqn (S1) are shown by the black lines. The individual fit components associated with the \( \tau_d \) and \( \tau_p \) time constants are shown by the bold red and dashed blue lines, respectively. No change to the amplitude of the \( \tau_d \) component is observed upon reducing the power density of the pump to \( \sim 1 \times 10^{10} \) W cm\(^{-2}\).

S4. Vapour-phase UV absorption spectrum of guaiacol

![UV absorption spectrum graph](image)

**Fig. S3** Vapour-phase UV absorption spectrum of guaiacol (grey) recorded over the range 210 – 300 nm. The \( S_1(v = 0) \) origin band of guaiacol is determined to lie at \( \sim 278 \) nm.\(^1\)\(^2\) The vapour-phase UV absorption spectrum of catechol is shown for comparison (black).
S5. Catechol$^+$ parent ion signal transients: $\lambda = 280.5 – 237$ nm

Fig. S4 Catechol$^+$ parent ion signal transients (open circles) recorded at many wavelengths over the range 280.5 – 237 nm. Associated kinetic fits to the data using eqn (S1) are indicated by the pink lines. Extracted time constants at each excitation wavelength are also provided.
S6. H⁺ signal transients (5000 – 8000 cm⁻¹): λ = 280.5 – 243 nm

Fig. S5 H⁺ signal transients obtained by integrating signal inTKER spectra over the range 5000 – 8000 cm⁻¹ at many Δt (open diamonds), over the excitation wavelength range 280.5 – 243 nm (where tunnelling dynamics are observed to be active). Kinetic fits to the transients using eqn (S2) (280.5 – 254 nm) and eqn (S3) (250 – 243 nm) are indicated by the red lines. Extracted τ₁ time constants are also provided.
S7. H⁺ signal transients (10000 – 14000 cm⁻¹): λ = 254 – 237 nm

Fig. S6 H⁺ signal transients obtained by integrating signal in TKER spectra over the range 10000 – 14000 cm⁻¹ at many Δt (open diamonds), over the excitation wavelength range 254 – 237 nm (where ultrafast O¹-H fission dynamics are observed to be active). Kinetic fits to the transients using eqn (S4) are indicated by the blue lines. Extracted τ_CI time constants are also provided.
S8. Vibrational modes of catechol’s S₁ excited electronic state

**Fig. S7** Calculated harmonic frequencies for catechol in its S₁ state at the CASSCF(10,8)/6-311+G(d,p) level. The eight lowest frequency modes are presented (labelled v₁ to v₈). All eight vibrations exhibit significant mode-mixed character, including O-H torsion and in- and out-of-plane motions.
Calculated harmonic frequencies for catechol in its $S_1$ state at the TD-CAM-B3LYP/6-311+G(d,p) level (frequencies were determined using a numerical frequency calculation). The eight lowest frequency modes are presented (labelled $v_1$ to $v_8$). As with the CASSCF(10,8)/6-311+G(d,p) calculated vibrations, all eight vibrations at the TD-CAM-B3LYP/6-311+G(d,p) level exhibit significant mode-mixed character, including O-H torsion and in- and out-of-plane motions.

**Fig. S8**
S9. Calculated minimum energy geometries of catechol’s S1 state

![Fig. S9 Minimum energy geometries of catechol’s S1 state (S1_min) at the (a) CASSCF(10,8) (b) TD-CAM-B3LYP (c) TD-M06HF and (d) TD-M062X levels of theory. All calculations utilised a 6-311+G(d,p) basis set.]

Calculations of the minimum energy geometries for the S1 state (S1_min) were performed using the Gaussian 09 computational suite, and are presented in Fig. S8. The structure calculated at the CASSCF(10,8)/6-311+G(d,p) level of theory is in good qualitative agreement with that reported in earlier studies by Gerhards et al., which also used the same (10,8) active space but with a smaller 6-31G(d,p) basis set. The ‘free’ O1-H bond is calculated to lie at an angle of ~16° degrees out of the phenyl ring plane, compared to ~24° at the CASSCF(10,8)/6-31G(d,p) level.

The structures determined using density functional response theory, with the CAM-B3LYP, M06HF and M062X functionals, are in good agreement with each other. Reassuringly, these calculated S1_min structures are very comparable to that previously determined at the RICC2/aug-cc-pVTZ level by Ashfold and co-workers. However, all response theory methods find that there is a significant out-of-plane distortion of the phenyl ring, as well as the C-O-H moieties, unlike the structure calculated at the CASSCF(10,8)/6-311+G(d,p) level. The precise origins of this discrepancy are currently unclear, although a lack of dynamic correlation effects in the CASSCF calculations may be one possible cause; further theoretical studies are required to investigate this in greater detail, but are beyond the scope on the present work. Nonetheless, both response theory and CASSCF calculations provide strong evidence that the S1_min structure of catechol is indeed non-planar.

S10. Determination of branching fractions (Γ')

The experimentally observed branching fraction (Γ) for S2 driven O1-H bond fission originating from tunnelling under the S1/S2 CI, at each excitation wavelength (λ) is determined using the time-resolved TKER spectra presented in Fig. 3 of the main article. Γ is formally defined as:
Fits (black lines) to TKER spectra recorded at $\Delta t = 1$ ps (grey line) at (a) 254, (b) 250, (c) 246 and (d) 243 nm. Fits are performed using eqn (S6) and the individual Gumbel (red lines) and Gaussian (blue lines) are also provided (see section S10 for details).

\[ \Gamma = \frac{\gamma_1}{(\gamma_1 + \gamma_2)}, \]

where $\gamma_1$ and $\gamma_2$ are the total integrated signals associated with $S_2$ mediated O-H fission originating from tunnelling under the $S_1/S_2$ CI and direct dissociation along the $S_2$ surface, respectively.

For wavelengths between 254 – 243 nm, $\gamma_1$ is determined by integrating the signal difference between TKER spectra recorded $\Delta t = 50$ ps and 1 ps (see red shading in Fig. 3 of main manuscript). Over the same wavelength range, $\gamma_2$ is determined by first fitting the profile of the TKER spectra at $\Delta t = 1$ ps, $I(x)$, to sum of a Gaussian and an extreme value (Gumbel) distribution, which have the functionality:

\[ I(x) = I_0 + \left[ A \exp\left( -\frac{(x-\mu_1)^2}{2\sigma_1^2} \right) \right] + \left[ B \exp\left( -\frac{(x-\mu_2)}{\sigma_2} \right) \exp\left( -\exp\left( -\frac{(x-\mu_2)}{\sigma_2} \right) \right) \right], \]

where $x$ is the TKER, $I_0$ is the baseline signal level, $A$ is the amplitude of the Gaussian function, $\sigma_1$ and $\mu_1$ are the width and centre of the Gaussian distribution, respectively, $B$ is the amplitude of the Gumbel function, and $\sigma_2$ and $\mu_2$ are the width and location parameters of
the Gumbel distribution. The results of these fits are shown in Fig. S10 as solid black lines overlaid on top of the recorded TKER spectrum (grey line). The Gumbel function is used to model the underlying two-colour background signal arising from undesired multiphoton processes (red line), while the Gaussian models the remaining contribution of H\(^+\) signal associated with ultrafast O\(^1\)-H fission dynamics resulting from direct excitation to the S\(_2\) surface (blue line). Values for \(\gamma_2\) are finally obtained by integrating the Gaussian component of these fits, which together with \(\gamma_1\), ultimately enable a determination of \(\Gamma\).

ESI References