Relaxation Dynamics of Photoexcited Resorcinol: Internal Conversion *versus* H atom Tunnelling

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Abstract

The excited state dynamics of resorcinol (1,3-dihydroxybenzene) following UV excitation at a range of pump wavelengths, $278 \geq \lambda \geq 255$ nm, have been investigated using a combination of time-resolved velocity map ion imaging and ultrafast time-resolved ion yield measurements coupled with complementary *ab initio* calculations. After excitation to the $1^1\pi\pi^*$ state we extract a timescale, τ_1, for excited state relaxation that decreases as a function of excitation energy from 2.70 ns to ~120 ps. This is assigned to competing relaxation mechanisms. Tunnelling beneath the $1^1\pi\pi^*/^1\pi\sigma^*$ conical intersection, followed by coupling onto the dissociative $^1\pi\sigma^*$ state, yields H atoms born with high kinetic energy (~5000 cm^{-1}). This mechanism is in competition with an internal conversion process that is able to transfer population from the photoexcited $1^1\pi\pi^*$ state back to a vibrationally excited ground state, S_0^*. When exciting between $264 - 260$ nm a second decay component, τ_2, is observed and we put forth several possible explanations as to the origins of τ_2, including conformer specific dynamics. Excitation with 237 nm light (above the $1^1\pi\pi^*/^1\pi\sigma^*$ conical intersection) yields high kinetic energy H atoms (~11000 cm^{-1}) produced in ~260 fs, in line with a mechanism involving direct dissociation from the $^1\pi\sigma^*$ state or ultrafast coupling between the $1^1\pi\pi^*$ (or $2^1\pi\pi^*$) and $^1\pi\sigma^*$ state followed by dissociation. The results presented above highlight the profound effect the presence of additional functional groups, and more specifically the precise location of the functional groups, can have on the excited state dynamics of model heteroaromatic systems following UV excitation.

1. Introduction

There are a great number of experimental and theoretical studies in the recent literature focusing on the excited state dynamics of heteroaromatic species,[1] with particular focus on the mechanisms by which population in the electronic excited states of these molecules undergoes relaxation back to the electronic ground state (S_0). One of the key driving forces behind this interest originates from the understanding that these molecules play an important role as ultraviolet (UV) chromophores in a multitude of larger biological species, such as the aromatic amino acids,[2] DNA bases[3-7] and (eu)melanin pigments.[8, 9] In an attempt to better understand the complex photochemistry and photophysics associated with these larger biomolecules, a 'bottom-up' approach has often been favoured,[10] particularly for studies conducted on isolated species in the gas phase. Notably, the relaxation pathways followed by smaller 'model' heteroatom-containing molecules such as phenols,[11-15] aromatic amines,[16-18] indoles[19-22] and imidazoles[23, 24] have been studied in detail. Phenols are one such class of these 'model' systems, and in this contribution we explore the deactivation mechanisms occurring upon UV excitation of resorcinol (1,3-dihydroxybenzene, structure shown inset in Figure 1) using a combination of ultrafast time-resolved velocity map ion imaging (TR-VMI) and time-resolved ion yield (TR-IY) experiments, in conjunction with high level *ab initio* calculations.

The general electronic excited state landscape of phenol (at least along the O-H bond coordinate, R_{O-H}) is, by now, well described.[25-27] It is widely accepted that an excited $^1\pi\pi^*$ state (herein labelled $1^1\pi\pi^*$) accounts for the first absorption onset in the UV absorption spectrum of most phenols, such as that shown in Figure 1 for resorcinol. An 'optically dark' $^1\pi\sigma^*$ state, which is dissociative with respect to R_{O-H}, lies above the $1^1\pi\pi^*$ state in the vertical Franck-Condon (vFC) excitation region, and it has been revealed, through a combination of both experiments and theory, that non-adiabatic interactions between the 'bright' $1^1\pi\pi^*$ state and 'dark' $^1\pi\sigma^*$ state, play a major role in the excited state relaxation dynamics of phenol and many of its derivatives.[1, 14, 15, 28] At extended R_{O-H} distances, the $^1\pi\sigma^*$ state

becomes degenerate with the $1^1\pi\pi^*$ state creating a $1^1\pi\pi^*/^1\pi\sigma^*$ conical intersection (CI). At energies above this CI population can, in principle, be transferred non-adiabatically from $1^1\pi\pi^* \rightarrow {}^1\pi\sigma^*$ on an ultrafast timescale. Once on the $^1\pi\sigma^*$ state, further extension of the O-H bond leads to another CI, formed between the $^1\pi\sigma^*$ and the ground S_0 state ($^1\pi\sigma^*/S_0$ CI). Non-adiabatic coupling through this $^1\pi\sigma^*/S_0$ CI allows the molecule to either transfer to a highly vibrationally excited S_0 state (S_0^*) or undergo O-H bond scission, the latter resulting in the production of high kinetic energy (KE) H atoms in association with radical co-fragments - in the specific case here, resorcinoxyl radicals ($C_6H_5O_2\bullet$).

Perhaps somewhat counter intuitively, excitation below the $1^1\pi\pi^*/^1\pi\sigma^*$ CI in phenol and many (but not all) of its derivatives still results in the formation of high KE H atoms.[27, 29, 30] This is a signature for $^1\pi\sigma^*$ driven O-H scission, occurring on a longer timescale, despite the considerable barrier to dissociation (~4000 cm^{-1} in phenol[26, 27]). It is now the general understanding that these high KE H atoms are borne through non-adiabatic coupling from the $1^1\pi\pi^*$ state onto the $^1\pi\sigma^*$ state by tunnelling beneath the $1^1\pi\pi^*/^1\pi\sigma^*$ CI. In phenol, Ashfold and co-workers concluded this process is mediated by a torsional motion of the phenyl ring, labelled the ν_{16a} mode in Wilson's notation,[26] although earlier theoretical treatments implied O-H torsion (τ_{OH}) should drive such behaviour.[31]

When compared to phenol itself, there are relatively few investigations reporting the excited state dynamics of its hydroxy-substituted derivatives: catechol (1,2-dihydroxybenzene), hydroquinone (1,4-dihydroxybenzene) and resorcinol. Only very recently have a number of more detailed investigations been performed to understand the excited state dynamics in these species, of which catechol has received the most attention.[12, 29, 32] Catechol was particularly notable, as although the dynamics observed in TR-VMI, TR-IY and time-resolved photoelectron imaging (TR-PEI) experiments could be qualitatively rationalized through a comparison with phenol, the tunnelling rate under the $1^1\pi\pi^*/^1\pi\sigma^*$ CI was found to be ~2 orders of magnitude greater (5 – 12 ps lifetime, $cf.$ >1 ns in phenol[27]), despite a similar barrier height to phenol along R_{O-H}. Such an observation was proposed to be a direct

consequence of the non-planar $1^1\pi\pi^*$ minimum energy geometry in catechol, yielding relaxed symmetry constraints for $1^1\pi\pi^* \rightarrow {}^1\pi\sigma^*$ coupling and a highly 'vibrationally-enhanced' tunnelling process.[29] Conversely, the minima of the $1^1\pi\pi^*$ states in hydroquinone and resorcinol are both planar, and the recent TR-PEI experiments by Livingstone *et al.* (after excitation at 267 nm only) found that both species exhibited relaxation dynamics more akin to phenol, identifying two time constants; a long time component, occurring on a timescale $\geq$430 ps, and a shorter sub-picosecond component.[12] The long time dynamics observed were assigned to population decaying out of the $1^1\pi\pi^*$ state, driven (at least in part) by tunnelling beneath the $1^1\pi\pi^*/{}^1\pi\sigma^*$ CI, while the latter rapid sub-picosecond component was ascribed to ultrafast intramolecular vibrational redistribution (IVR) mediated by 'doorway' states on the $1^1\pi\pi^*$ surface. In the specific case of resorcinol, the lifetime of the $1^1\pi\pi^*$ state extracted from the time-resolved photoelectron spectrum at 267 nm was given as >1 ns and the authors noted that they could not make a more reliable estimate for the lifetime based on the temporal limits of their experimental setup.

As well as the above study in the time-domain, high resolution microwave and electronic spectroscopy, coupled with *ab initio* calculations, have also been performed on resorcinol.[12, 33-35] It has been proposed that resorcinol may exist in three possible conformations, brought about by variation in the orientations of the OH groups (labelled A-C in Figure 1), although only two of these have been spectroscopically observed in the gas phase under jet expansion conditions. These two conformers, labelled A and B in Figure 1, are nearly iso-energetic, separated only by ~10 cm^{-1}.[35] Using spectral-hole burning, Gerhards *et al.* were able to identify two transitions at 35944 cm^{-1} (278.2 nm) and 36196 cm^{-1} (276.3 nm), and assigned them to the $1^1\pi\pi^* \leftarrow S_0$ origin bands for the A and B conformers, respectively.[35] Further high resolution dispersed fluorescence spectroscopy studies on isotopically substituted resorcinol, its cations and the molecule itself have yielded a greater understanding of the structure and vibrations in the S_0, $1^1\pi\pi^*$ and cation electronic states.[33-35]

With the exception of the TR-PEI work conducted by Livingstone *et al.* at 267 nm,[12] there have, to the best of our knowledge, been no other studies investigating the dynamics that take place within photoexcited resorcinol in the time-domain. To this end, we present here the first comprehensive study of the relaxation dynamics of resorcinol after photoexcitation at a number of wavelengths across the range 278 – 237 nm, using a combination of TR-VMI and TR-IY experiments, in conjunction with detailed theoretical calculations using the complete-active space self-consistent field (CASSCF) method together with its second order perturbation theory extension (CASPT2).

2. Methods

2.1 Experimental

The experiment has been described in greater detail elsewhere,[36, 37] and as such only a brief overview is given here. Femtosecond (fs) laser pulses are generated by a commercial fs Ti:sapphire oscillator and regenerative amplifier (Spectra-Physics Tsunami and Spitfire XP, respectively), outputting ~40 fs pulses centred at 800 nm (~3 mJ/pulse). The fundamental output is subsequently split into three beams (~1 mJ/pulse), two of which are used to pump two separate optical parametric amplifiers (Light Conversion, TOPAS-C) in order to generate the pump ($h\nu_{pu}$) and probe ($h\nu_{pr}$) pulses. $h\nu_{pu}$ is tunable in the range 278 – 255 nm (~2.5 – 5 µJ/pulse) and $h\nu_{pr}$ is fixed at 243 nm (~6 µJ/pulse) in line with the two photon allowed 2s ← 1s transition in H. The pump and probe pulses are temporally delayed with respect to each other by passing the probe beam through a hollow gold retroreflector mounted on a motorized delay stage, allowing a maximum temporal delay (Δt) of 1.2 ns. The two beams are focussed near-collinearly into the interaction region (10^{-8} mbar) of a vacuum chamber where they perpendicularly intersect a molecular beam seeded with the target molecule.

The molecular beam is produced by seeding resorcinol (Sigma-Aldrich, 99%) or resorcinol-d_2, (synthesised by dissolving resorcinol in D_2O, stirring and then evaporating the excess heavy water using a rotary evaporator), heated to 100 °C, into helium (~2 bar). Seeded molecular beam pulses are

then generated using an Even-Lavie pulsed solenoid valve[38] operating at a 125 Hz repetition rate with a typical opening time of 14 μs. The seeded gas pulses pass from the source region (10^{-6} mbar) through a 2 mm skimmer into the interaction region which contains the VMI optics. Non-resonant multiphoton ionisation of methanol is used to measure the delay position corresponding to temporal overlap of $h\nu_{pu}$ and $h\nu_{pr}$ pulses ($\Delta t = 0$), to within an accuracy of ±15 fs. The Gaussian cross-correlation/instrument response function (IRF) was also determined using this method, yielding a value of ~120 fs full width at half maximum (FWHM).

At the point of intersection, following photolysis by $h\nu_{pu}$, the resulting H atoms are probed using VMI. Firstly, the H atoms are ionised by the $h\nu_{pr}$ pulses forming H^{+}. The 3-D velocity distribution of H^{+} is then focused using a set of three ion optics, mirroring the set up described by Eppink and Parker,[39] onto a position sensitive detector which consists of a pair of micro-channel plates (MCPs) coupled to a P-43 phosphor screen (Photek, VID-240). The rear MCP is gated using a timed voltage pulse in order to detect only H^{+} (1 amu). The photoemission from the phosphor screen is captured using a CCD camera (Basler, A-312f) and the 3-D distribution is reconstructed from the collected 2-D image using a polar onion peeling (POP) algorithm.[40] By radially integrating a slice from the centre of the reconstructed image, it is possible to produce a total kinetic energy release (TKER) spectrum by using an appropriate Jacobian, calibration factor and consideration of the co-fragments mass. The calibration factor is measured using the known TKER spectrum of HBr recorded at 200 nm.[41]

In addition to TR-VMI measurements, the spectrometer is capable of recording TR-IY measurements of the resorcinol parent cation with an appropriately widened detector gate. Additionally, the gas phase absorption spectrum of resorcinol in Figure 1 was recorded over the range 210 – 300 nm using a commercially available UV-visible spectrometer (Perkin-Elmer, Lambda 25, 0.2 nm resolution). The spectrum was recorded by placing a small mass of resorcinol into a fused silica sample cell and heating to ~80˚C in order to obtain sufficient vapour pressure.

2.2 Theoretical methods

Vertical excitation energies were calculated using both Gaussian[42, 43] and Molpro computational suites.[44] Density functional theory (DFT) was used to perform all geometry optimisations with the PBE0[45] functional, together with the aug-cc-pVTZ basis set. For geometry optimised structures of conformers A and B (see Figure 1), both equation-of-motion coupled cluster with single and double excitations (EOM-CCSD[46]) and time-dependent density functional theory with the PBE0 functional (TD-PBE0) were then used to calculate vertical excitation energies (ΔE_{vert}) of the $1^1\pi\pi^*$, $2^1\pi\pi^*$ and $^1\pi\sigma^*_{O^n-H}$ states. The aug-cc-pVDZ and aug-cc-pVTZ basis set was used for the EOM-CCSD and TD-PBE0 calculations, respectively. Torsional barriers to inter-conversion between conformers A/B and A/C were determined at the PBE0/aug-cc-pVTZ level in the S_0 ground state. At each torsional angle (θ), θ was held fixed and the remaining nuclear coordinates were allowed to 'relax'. Insight into the torsional barriers in the $1^1\pi\pi^*$ state are determined by calculating the vertical excitation energies at the TD-PBE0/aug-cc-pVTZ level for each point along the 'relaxed' torsional coordinates in the S_0 state. Bond dissociation energies (D_0) were computed by performing ground state geometry optimisations on the two conformers as well as the two possible radical products produced following dissociation of the O^n-H bond. The PBE0 functional was used with an aug-cc-pVTZ basis set. Zero point energy corrections were applied in all cases, extracted from frequency calculations performed to the same level of theory. The PBE0 functional has been selected since a recent survey of functionals for performing TD-DFT, by Leang et al.,[47] has indicated the PBE0 functional provides the most balanced description of both valence and Rydberg excited electronic states (both of which are important here in resorcinol), when benchmarked against experimental measurements. All TD-DFT and EOM-CCSD calculations were performed using the Gaussian09 computational suite.

Minimum energy crossing point (MECPs) structures and two-dimensional branching spaces for conical intersections (CIs) in resorcinol were calculated using the CASSCF method with the 6-31G*

basis set. For CIs involving excited $^1\pi\sigma^*_{O^n\text{-H}}$ surfaces, a 12 electrons in 10 orbitals (12,10) active space was used consisting of the three π bonding orbitals, the two n_π non-bonding orbitals associated with the O atoms (conjugated into ring π-system), the three π^* anti-bonding orbitals and the corresponding σ bonding and σ^* anti-bonding orbitals associated with the given O^n-H bond coordinate of interest. A smaller (10,8) active, excluding the σ and σ^* orbitals associated with the O^n-H bond, was used to isolate MECPs for CIs between $1^1\pi\pi^*/S_0$ and $2^1\pi\pi^*/1^1\pi\pi^*$ electronic states. Analytical gradient driven techniques were used to locate all MECPs of the CI seams, using the method described by Robb and co-workers,[48] as implemented in Gaussian03. Solutions to the coupled-perturbed multi-configurational self-consistent field (CP-MCSCF) equations in state-averaged CI optimizations were approximated by neglecting orbital rotation derivatives.

Molpro calculations were performed using CASPT2 theory[49, 50] with a 12 electrons in 12 orbitals (12,12) active space and the aug-cc-pVTZ basis set. Further geometry optimization was performed using CASSCF(12,12) theory[51, 52] as implemented in Gaussian03 with the same basis. In addition to the orbitals described above for the (12,10) active space, the two lowest lying 3s Rydberg orbitals associated with the O atoms were included in the larger (12,12) active space. The Rydberg orbitals were identified by looking for a large 3s component (smallest exponent on s-type basis function centred on oxygen) in the original Hartree-Fock ground state guess orbitals.

The potential energy cuts (PECs) of the excited and ground electronic states of the two active conformers of resorcinol were calculated using CASPT2 performed with Molpro. As before, geometry optimization was first performed using CASSCF with a (12,12) active space and the aug-cc-pVTZ basis set. PECs were produced along all three O-H coordinates (two coordinates in the A conformer and a single coordinate in B due to symmetry considerations – see structures in Figure 1). The bond was extended from the ground state equilibrium position to a distance of 4 Å (at which point the surfaces become asymptotic) then stepped back to 0.6 Å at varying intervals of internuclear separation,

R. Energies for each of the levels, S_0, $1^1\pi\pi^*$, $^1\pi\sigma^*$, and the lowest Rydberg state were then calculated for each step. At each point, only the O-H bond length was altered, all other geometric parameters being held constant, resulting in unrelaxed PECs.

3. Results and analysis

3.1 *Ab initio* calculations

a. Vertical excitation energies and torsional barriers

Table 1 collates the vertical excitation energies, resulting from TD-PBE0, EOM-CCSD and CASPT2 calculations, as well as the oscillator strengths (*f*) from the TD-PBE0 and EOM-CCSD. An experimental value for the $1^1\pi\pi^*$ origin is also included for comparison. Reasonable agreement can be seen between the TD-PBE0 and EOM-CCSD calculations, with the EOM-CCSD vertical excitation values more closely matching experiment, although still over estimating the $1^1\pi\pi^*$ origin by ~0.53 eV. The vertical excitation value for the first excited state as extracted *via* CASPT2 calculations follow the experimental values much more closely, giving a difference of < 0.01 eV for conformer A and ~0.06 eV for conformer B. Table 1 also shows the bond dissociation energies (D_0) for each of the three possible O–H coordinates across the two conformers (A and B) present in the molecular beam. The O^1–H coordinate has the lowest D_0 value, followed by the O^2–H and finally the O^3–H coordinate (see Figure 1 for O-H coordinate labels), calculated at the PBE0/aug-cc-pVTZ level of theory. Further TD-PBE0/aug-cc-pVTZ calculations were also performed to determined the torsional barriers to interconversion between conformers A/B and A/C in the excited $1^1\pi\pi^*$ state, returning barrier heights of 2126 cm^{-1} and 1980 cm^{-1} (relative to the $1^1\pi\pi^*$ origin) for switching between conformers A/B and A/C, respectively (not presented in Table 1).

b. Potential energy cuts and conical intersections

The PECs for the three pertinent O-H coordinates ($R_{O^n\text{-H}}$) are shown in Figure 2. These cuts demonstrate the dissociative nature of the $^1\pi\sigma^*$ state(s) with characteristics similar to those seen in

other phenol derivatives.[26, 27] In all three O–H stretch coordinates, a barrier is formed *via* a CI between the $1^1\pi\pi^*$ and $^1\pi\sigma^*$ states which must be overcome, or tunnelled through, for dissociation to occur. This barrier height is lowest along the O^1-H coordinate, having a value of 5330 cm^{-1}. The barrier heights to H atom tunnelling along the O^2-H and O^3-H coordinates are 6590 cm^{-1} and 6017 cm^{-1}, respectively. Calculations for tunnelling probabilities were performed based on the CASPT2 PECs using the Wentzel-Kramers-Broullian (WKB) method,[53] producing values of 1.2×10^{-3}, 1.9×10^{-5} and 2.1×10^{-4} respectively. We return to discuss the potential significance of these tunnelling probabilities in Section 4.

Continuing to follow increasing O–H bond lengths, once through the barrier a second CI is formed between the $^1\pi\sigma^*$ and S_0 states which allows dissociation through either adiabatic (in the A state of the $C_6H_5O_2$ radical, plus an H atom) or non-adiabatic (to the ground X state in the $C_6H_5O_2$ radical, plus an H atom) pathways. IC can also occur at the CI back to the ground state of the parent molecule, in which case dissociation will not occur. It should be noted that the O^2-H and O^3-H coordinates should converge to the same radical states. However, this is not the case here and is attributed to the unrelaxed nature of the calculations performed. This has been verified by performing geometry optimizations, at the TD-PBE0/aug-cc-pVTZ level, on the two radical products which do indeed optimize to the same asymptote.

Also presented in Figure 2 are the calculated gradient difference (GD) and derivative coupling (DC) branching space motions associated with the minimum energy crossing points (MECPs) of the CIs. These pairs of branching motions are the two nuclear motions responsible for lifting the energetic degeneracy between the two electronic surfaces at the MECPs of the CIs while the electronic state degeneracy is conserved in the remaining $3N$-8 vibrational degrees of freedom, where N is the number of atoms.[54, 55] The two modes correspond to the gradient of the energy difference between the two electronic states and the derivative coupling which is parallel to the non-adiabatic coupling gradient,

the latter of which is typically responsible for driving non-adiabatic (vibronic) coupling between the two electronic states and leading to population transfer through the CI.[55] Interestingly, unlike phenol, which conforms to a non-rigid G_4 (isomorphous with C_{2v}) symmetry due to torsional tunnelling,[56, 57] such symmetry constraints are not applicable in resorcinol, an observation that has also been noted in a recent study on 4-substituted phenols.[58] As a result, the lower C_s symmetry of both conformers A and B at extended O-H distances means that non-adiabatic coupling is driven by O-H torsional motion (rather than the ν_{16a} vibration, as posited in phenol[26, 58]), as evidenced in the branching space motions for both the $1^1\pi\pi^*/^1\pi\sigma^*$ and $^1\pi\sigma^*/S_0$ CIs along O^1-H in Figs. 2(b) and (c), respectively. A similar branching space is observed for these CIs along the O^2-H and O^3-H coordinates.

In addition to the CIs involving the $^1\pi\sigma^*$ states, CASSCF calculation with a smaller (10,8) active space also locate CIs between the $2^1\pi\pi^*$, $1^1\pi\pi^*$ and S_0 surfaces, which lie along coordinates orthogonal to O-H stretch coordinates presented in Fig. 2(a). In Fig. 2(d) the MECP of a prefulvenic-type CI, which links the $1^1\pi\pi^*$ and S_0 states, in presented. The calculated branching spaces are akin to those previous determined for the prefulvene CI in benzene, which is responsible for the so-called 'channel 3' decay pathway.[59] The CI structure presented in Fig. 2(d) is the lowest energy of a number of prefulvenic-type CIs that we have identified in resorcinol (varying in the location of the characteristic 'C-H kink' on the phenyl ring and the relative orientations of the O-H groups), all of which lie between ~7000-8000 cm^{-1} above the $1^1\pi\pi^*$ origin at the CASSCF(10,8)/6-31G* level. For comparison, the prefulvene CI in phenol was previously calculated to lie ~6400 cm^{-1} above the $1^1\pi\pi^*$ origin at the MRCI/aug-cc-pVDZ level.[31] Finally, Fig. 2(e) presents the MECP of a CI between the $2^1\pi\pi^*$ and $1^1\pi\pi^*$ states. The structure of this MECP and associated branching space motions are similar to a $2^1\pi\pi^*/1^1\pi\pi^*$ CI identified in another heteroaromatic species, aniline (aminobenzene),[17] and as in that case, may offer a pathway for rapid population transfer from $2^1\pi\pi^*$ to $1^1\pi\pi^*$.

3.2 Time-resolved ion yield: $\lambda = 278 - 255$ nm

a. Resorcinol

TR-IY experiments provide insight into the dynamics that take place in the excited state following excitation with UV radiation. By probing the parent resorcinol$^+$ ion as a function of Δt, we are able to observe the $1^1\pi\pi^*$ population decay (from the vertical Franck−Condon window) through all available relaxation pathways (e.g., fluorescence, IC, tunnelling, etc.) and, with reference to the above theoretical work, provisionally assign the origins of the measured lifetimes.

The left column of Figure 3(a)-(f) shows the resorcinol$^+$ signal transients obtained from TR-IY experiments (open circles). Upon cursory inspection it can be seen that each of the transients possess an initial sharp rise followed by an exponential decay. Where the temporal limit of the experiment has been sufficient to span the entire $1^1\pi\pi^*$ lifetime, the decay returns asymptotically to the baseline. In order to extract time constants for the $1^1\pi\pi^*$ lifetime from each transient, a kinetic fit was performed (blue line), consisting of an exponential decay function convoluted with our Gaussian IRF (~120 fs FWHM). Further information regarding our fitting procedures can be found in reference 29. It can be seen from the fits that the transients are mono-exponential, with the exception of the 264 and 260 nm transients (Figure 3(d) and (e)), providing us with a time-constant for the lifetime of the $1^1\pi\pi^*$ state (τ_1). The transients at pump wavelengths 264 and 260 nm required a bi-exponential decay in order to be fit accurately, producing two time-constants within the kinetic fit, τ_1 and τ_2, the origins of which we discuss in further detail below.

Simply by analogy with previous work,[12, 26, 29] one would be inclined to assign τ_1 to correspond to population decay *via* a tunnelling mechanism following the $1^1\pi\pi^* \rightarrow {}^1\pi\sigma^* \rightarrow C_6H_5O_2(X) + H$ pathway. At $1^1\pi\pi^*(v=0)$, we observe a timescale of $\tau_1 = $ ~2.7 ns which is certainly within the timescales one would expect when compared with the tunnelling timescale determined experimentally for phenol (~2.4 ns from reference 60). However, were tunnelling the only process by which

population could be removed from $1^1\pi\pi^*$, we might expect τ_1 to remain independent of excitation energy (see section 3.3a below).[27] Contrary to this however, as the excess energy imparted into the system increases (increasing $h\nu_{pu}$), we see a concurrent decrease in the $1^1\pi\pi^*$ lifetime by approximately one order of magnitude as the pump wavelength decreases from 278 – 255 nm. Behaviour akin to this was also observed in TR-IY experiments performed on parent phenol[+] and was assigned to a process wherein population was transferred back to the vibrationally excited ground state, termed S_0^*, by internal conversion (IC).[27] The fact that we see a decrease in τ_1 with decreasing wavelength is consistent with an IVR driven IC process following a Fermi's golden rule like argument.[61] We return to discuss this latter point in section 4 below.

b. Resorcinol-d_2

As well as the TR-IY data collected for resorcinol, we also performed complementary investigations on the doubly deuterated species, resorcinol-d_2. Figure 3(g)-(l) shows the 243 nm probed [resorcinol-d_2][+] parent ion as a function of Δt for the same range of wavelengths as those studied in non-deuterated resorcinol. It can be seen that the curves display the same basic behaviour as was observed in non-deuterated resorcinol; an initial sharp rise ($\Delta t = 0$) which then decays exponentially with some lifetime, τ_3, which decreases with increasing energy. Values were extracted for τ_3 *via* the application of kinetic fits as described previously (section 3.2a).

For all wavelengths investigated, τ_3 is slower than, or comparable to, τ_1 within the error of the fits. This behaviour is consistent with the $1^1\pi\pi^*$ state in non-deuterated resorcinol decaying *via* competing mechanisms including tunnelling; the increased mass of the D atom significantly reduces the tunnelling probability (*cf.* phenol[26, 27]) compared to H atom tunnelling, effectively deactivating this relaxation channel from the $1^1\pi\pi^*$ state. At higher excitation energies the values for τ_3 in general become more comparable to the τ_1 value for the equivalent wavelength as, at these energies, the rate of IC is significantly greater than that of tunnelling and so the $1^1\pi\pi^*$ lifetime is relatively unaffected by

the deactivation of the tunnelling pathway.

Perhaps the most striking difference brought about by deuteration is that every transient is now mono-exponential in nature, requiring only one time constant in order to fit the long decay accurately. This allows us to suggest that whatever process is responsible for τ_2 is made orders of magnitude slower, or turned off entirely, by deuteration of the sample, possibly suggesting a second tunnelling mechanism is accessible at these energies. We return to discuss the origins of each of the discussed time constants in further detail in section 4.

3.3 Time-resolved H$^+$ velocity map imaging: λ = 278 – 255 nm

a. TKER spectra

Figure 4 shows the TKER data collected over a probe wavelength range of 278 – 255 nm (filled circles), as derived from H$^+$ images such as the 273 nm example shown inset, following excitation to the 1$^1\pi\pi^*$ state. All spectra and images were recorded at Δt = 1.2 ns. In order to remove unwanted one colour contributions, an image collected at negative time, corresponding to the pump alone and probe alone signals, is subtracted from each image. The left half of the example image shows the subtracted REMPI probed H$^+$ data, while the right half shows the same image after deconvolution with the POP algorithm. From the deconvoluted image we can see the dominant contribution is a single, high intensity ring at large radii which is isotropic with respect to the pump laser polarisation (ε), as shown by the white arrow. The isotropic nature of this feature is suggestive of H atom elimination occurring on a timescale slower than the time required for rotational dephasing. As mentioned above, from the collected H$^+$ images we can extract corresponding TKER spectra, as plotted in Figure 4(a)-(f). Each spectrum exhibits two distinct features - a low TKER, 'Boltzmann like' distribution and a higher energy Gaussian signal. These two features are highlighted by the fits applied to the 278 nm spectrum: the green line represents the Boltzmann background and the black line is the Gaussian contribution. The lower lying signal has been assigned previously in related heteroaromatic species to statistical or

multiphoton processes.[27, 62] This feature is not the focus of this work and as such shall not be discussed further. We turn our attention instead to the signal at high (~5000 cm^{-1}) TKER. A well-defined Gaussian signal such as this is characteristic of H atoms produced by $^1\pi\sigma^*$ mediated processes, as has been observed in previous experiments.[15, 28, 63, 64] By analogy with phenol and catechol, we provisionally assign the appearance of this signal to dissociation along the $^1\pi\sigma^*$ state preceded by tunnelling beneath the $1^1\pi\pi^*/^1\pi\sigma^*$ CI.

In order to further elucidate as to whether this feature is indeed related to dissociation along the R_{O-H} coordinate, we can consider the energetics of the dissociation process. Due to the presence of the two separate conformers, it is possible that all 3 O^n-H coordinates are able to dissociate in order to produce H atoms. By taking the O^1-H coordinate value for D_0, as calculated using the PBE0 functional (~28930 cm^{-1}), we are able to calculate a value for the theoretical maximum kinetic energy for H atoms born through an R_{O-H} dissociation process. For each of the pump wavelengths, the calculated TKER$_{max}$ is shown by the small black arrow above the spectra. At the $1^1\pi\pi^*$ origin (278 nm) a photon energy, $h\nu_{pu}$, of 35971 cm^{-1} yields an estimated TKER$_{max}$ of ~7000 cm^{-1} in line with the observed TKER cut-off point. As the amount of excess energy imparted into the system increases, we might expect that the TKER$_{max}$ increases in the same manner, however, we see very little difference in the spectra. There is only a very slight shift (~500 cm^{-1}) in the TKER of maximum intensity between 278 and 255 nm. Similar behaviour was witnessed in phenol and catechol, and was ascribed to a mechanism wherein tunnelling occurs solely from the zero-point energy (ZPE) of the $1^1\pi\pi^*$ state, while the majority of the excess energy occupies vibrational "spectator" modes, orthogonal to the R_{O-H} coordinate.[27, 29] The above evidence leads us to assign the origins of this high TKER signal to the appearance of H atoms born *via* tunnelling beneath the $1^1\pi\pi^*/^1\pi\sigma^*$ CI as concluded by Livingston *et al.* in their earlier TR-PEI experiments.[12]

It is also worth noting that as a function of increasing $h\nu_{pu}$, we see a large decrease in signal to noise

ratio of the recorded images. It is likely that this decrease in H-atom signal is a result of a corresponding decrease in the quantum yield for H atoms born through dissociative processes at shorter wavelengths, coupled with a decreasing photoabsorption cross-section. We believe this is another possible indication that the process by which O-H bond rupture occurs is in direct competition with a non-dissociative process, such as IC, that is capable of removing population from $1^1\pi\pi^*$ before tunnelling onto S_2 can take place. This complements the conclusions drawn from the TR-IY experiments in section 3.2, showing that IC is in fact an important relaxation process that is in direct competition with the tunnelling mechanism.

b. H^+ signal transients

By collecting a series of TKER spectra as a function of Δt between -1 ps and 1.2 ns and integrating over the relevant TKER range, we are able to produce time-resolved plots for the appearance of a particular feature. Figure 5 shows normalised H^+ signal transients generated by integrating the TKER signal over the range 3000–8000 cm^{-1} (open circles) for all wavelengths studied. As described above, the image at each Δt has a negative time image subtracted before deconvolution, to remove unwanted one-colour signal. Each transient has the same basic structure; before $\Delta t = 0$ the probe beam precedes the pump beam and we observe very little H^+ signal, in line with the fact that the pump is unable to resonantly ionise any released H atoms. At $\Delta t = 0$ we see a sharp rise and decay (<1 ps) corresponding to the appearance of the small multiphoton background signal, as seen in our example H^+ image (Figure 4, inset), and finally, a slow (>100 ps) exponential rise at long times, assigned to the appearance of the high TKER H atoms formed through a $1^1\pi\pi^* \rightarrow {}^1\pi\sigma^* \rightarrow C_6H_5O_2(X) + H$ pathway *via* tunnelling below the $1^1\pi\pi^*/^1\pi\sigma^*$ CI.

Again, we can apply kinetic fits to the recorded data in order to acquire values for the timescale of the ensuing H atom dynamics. In this case each fit consists of two exponential rise functions and one exponential decay function. The sharp rise and decay functions correspond to the faster multiphoton

signal. The slow rise function corresponds to the appearance of high KE H atoms. All functions are convolved with our IRF. It is worth noting that, for the two longest wavelengths recorded, 278 and 273 nm, the dynamics are incomplete within the temporal limit of our experiments (~1.2 ns) and so, in order to provide an approximate value for the lifetime, these transients have restricted fits applied to them (blue, dotted line) using the decay timescale acquired from the parent ion at these wavelengths (see Figure 3). The remaining wavelengths, 268 – 255 nm, begin to, or plateau inside, the experimental temporal window and as such are entirely free fit (red, solid line).

The time constant (τ_H) for the high TKER component extracted from the kinetic fits is shown in red next to the relevant transient. The decrease in lifetime of O-H bond scission, evident from these results, agrees favourably with the decrease in τ_1 seen in the TR-IY experiments (section 3.1). This increased rate of H atom production, in conjunction with the decrease in quantum yield witnessed in the TKER spectra, further supports our proposal that we are observing competing deactivation mechanisms. In previous studies on phenol, such a correlation between TR-IY measurements of the phenol$^+$ transient and the rate of H atom production was not evident. Indeed, H$^+$ transients modelled by a constant value for the rate of H atom production resulted in a reasonable (within signal-to-noise) fit, irrespective of increasing excitation energy. The phenol$^+$ transients, however, displayed a decreasing time constant as expected. Retrospectively, we attribute this to combined effects: (1) The poor signal to noise of our H$^+$ transients, especially at the shorter excitation wavelengths where the absorption cross-section falls considerably in contrast to the much improved signal-to-noise attained in resorcinol. (2) The fact that none of the H$^+$ transients in phenol were showing any conclusive evidence of H$^+$ signal plateauing within the temporal window of the experiment, whereas this is only apparent for the two lowest energy transients in resorcinol. (3) The reduced rate of increase in density of states (see section 4) in phenol within the excitation wavelength range. Both (1) and (2) have enabled us to extract more reliable time constants, τ_H, from resorcinol, which follows τ_1 whilst (3) may tentatively suggest

why the decreasing time constants extracted from phenol[+] transients are not as pronounced as in resorcinol[+] transients to strongly influence the associated H^{+} transients. Combined, the H^{+} transients in phenol do not show as marked a change in the H atom production with increasing excitation energy.

3.4 Time-resolved H^{+} velocity map imaging: λ = 237 nm

Following excitation at 237 nm (5.23 eV) we see a new relaxation pathway become accessible. As can be seen from Figure 1, at these energies, a new absorption feature begins to appear, likely corresponding to the onset of the $2^1\pi\pi^*$ state (see Table 1). While we calculate the vertical excitation energy of this state to be 5.64 eV at the CASPT2 level, the $2^1\pi\pi^*$ state will likely have a significantly different minimum energy geometry to that of the S_0 state, resulting in some minimal absorption cross-section extending into longer wavelengths (*cf.* findings from previous studies on *para*-methoxyphenol[15] and aniline[17]). Figure 6 shows an H^{+} image (inset (a)) and TKER spectrum (a) collected at Δt = 100 ps following photoexcitation with λ_{pu} = 237 nm. As with images and spectra collected at longer wavelengths, both have had a background image subtracted in order to remove any unwanted one-colour signal. The image is much the same as seen previously, consisting of a "noisy" central signal and a higher intensity ring at larger radii. The key difference at this wavelength is that the high intensity ring appears at a larger radius than observed previously. This implies that H atoms are being generated with higher KE compared to excitation below the $1^1\pi\pi^*/^1\pi\sigma^*$ CI, allowing us to preliminarily suggest that O-H bond dissociation occurs from a higher lying excited state.

The structure of the spectrum is qualitatively similar to that seen for the lower excitation energies; a broad Boltzmann-like background, extending across the entire spectrum, and a higher lying Gaussian signal at ~11000 cm^{-1}. Similarly to previous arguments, the presence of a broad symmetric Gaussian signal at high TKER is often indicative of H atoms formed through $^1\pi\sigma^*$ driven processes. To verify this we must refer once again to the PECs in section 3.1b.

On energetic grounds, when exciting with 237 nm light (~6200 cm^{-1} above the $1^1\pi\pi^*$ origin), the

PECs indicate that we are exciting to the region close to the dissociative $^1\pi\sigma^*$ state (~8000 cm^{-1} above the $1^1\pi\pi^*$ origin). Once again, we can calculate the theoretical TKER$_{max}$ for a feature arising from this point on the potential curve. Following excitation with $h\nu_{pu}$ = 42194 cm^{-1}, the calculation yields a TKER$_{max}$ value of ~13500 cm^{-1} which is in excellent agreement with the TKER cut off point for the high TKER feature.

The H$^+$ signal transient for this feature, integrated over 8000 – 14000 cm^{-1}, is shown in Figure 6b. An extracted timescale of 260 fs indicates the presence of an ultrafast process such as direct dissociation from the $^1\pi\sigma^*$ state or ultrafast coupling between the $1^1\pi\pi^*$ (or higher lying $2^1\pi\pi^*$ state) and $^1\pi\sigma^*$ state followed by dissociation, mediated by the appropriate CIs shown in Fig. 2. This compares very favourably with the results for excitation above the $1^1\pi\pi^*/^1\pi\sigma^*$ CI witnessed in catechol.[29]

Interestingly, another feature observed in the TKER spectrum is a second, much less intense Gaussian signal centred at ~4200 cm^{-1}. It is tentatively suggested that this feature corresponds to H atoms formed in conjunction with excited A state resorcinoxyl radicals (see Figure 2). This conclusion is supported by consideration of the energetics for this dissociation channel. The experimentally measured splitting between the A and X states of the resorcinoxyl radical is 8100 cm^{-1},[65] returning a predicted TKER$_{max}$ of ~5200 cm^{-1} for the A state channel (vertical red arrow in Figure 6), in excellent agreement with the location of the smaller Gaussian feature. Unfortunately we were unable to extract a transient from this peak due to both the poor signal-to-noise and the overlapping Boltzmann and Gaussian feature arising from the X state radical.

4. Discussion

4.1 Competing dynamics

It was seen in the TR-IY experiments that the rate of population transfer from the $1^1\pi\pi^*$ excited state is highly dependent on the excitation energy. As mentioned previously, this is as we might expect for

an IVR driven IC process following a Fermi's golden rule-like argument. In terms of the system in question, the density of vibrational states (DOS) in the final S_0^* state in the IC process (as would normally be the case in Fermi's golden rule), will be relatively constant across our excitation window (278 – 255 nm) and have little impact on the rate of IC. Instead, we consider the DOS in the excited $1^1\pi\pi^*$ state (presented in Figure 7). As $h\nu_{pu}$ increases, the DOS accessed in $1^1\pi\pi^*$ grows, resulting in a greater propensity for IVR into out-of-plane vibrational modes which can more efficiently promote IC back to S_0^* and reduce the overall $1^1\pi\pi^*$ lifetime. This appears to be akin to the well-known 'channel 3' decay mechanism in benzene, which possesses an onset at ~3000 cm^{-1} above its $1^1\pi\pi^*$ state origin.[66-69] Indeed, the deviation of the lifetime at λ_{pu} = 255 nm (~3200 cm^{-1} excess internal energy in $1^1\pi\pi^*$) from a simple logarithmic progression here in resorcinol may be due to an analogous 'channel 3'-like decay process, driving population towards a prefulvenic $1^1\pi\pi^*/S_0$ CI, such as that presented in Fig. 2(d). However, it should be noted that time-resolved studies in benzene have shown that this mechanism generally manifests itself with lifetimes on the order of picoseconds or sub-picoseconds,[70-73] whereas the excited $1^1\pi\pi^*$ state lifetime observed in these studies is never less than hundreds of picoseconds - orders of magnitude slower than in benzene. Nevertheless, from these arguments we can tentatively assign τ_1 to a $1^1\pi\pi^*$ decay process involving competing dynamics between H atom tunnelling and IVR driven IC.

In an attempt to verify this argument, Figure 7 shows a comparison plot of the DOS in the $1^1\pi\pi^*$ state for resorcinol and the rate of $1^1\pi\pi^*$ depopulation as a function of excess internal energy in $1^1\pi\pi^*$ (E_{vib}). The DOS in the $1^1\pi\pi^*$ state, were derived from the calculated CASSCF harmonic frequencies in $1^1\pi\pi^*$ using an extended Beyer-Swinehart method described in reference 74. k_x represents the rate of depopulation through the different identified pathways; $1/\tau_1$ (blue circles), $1/\tau_2$ (black diamonds) and $1/\tau_H$ (red squares). As stated previously τ_1 and τ_H compare very well and, for the most part, there is a reasonable correlation between both k_1 and k_H and the calculated DOS for either conformer (shown by

the solid blue and red lines). This leads us to assume that we are observing a DOS driven process which, in this specific case, is most likely to be IVR driven IC back to the electronic ground state. The above evidence, coupled with our arguments made in section 3.3, further supports our postulate that τ_1 is a combination of IC, in direct competition with H atom tunnelling.

Figure 7 also presents the DOS calculated for phenol in $1^1\pi\pi*$ (grey dashed line). The rate of increase of DOS with increasing excess energy is greatly reduced compared to that of either resorcinol conformer. As such, the increase in the rate of IC is likely to be less pronounced in phenol, which accords well with our observation of longer excited state lifetimes extracted from TR-IY measurements of the parent phenol$^+$ transient.[27] As such, the $1^1\pi\pi*$ lifetime would appear to remain constant within our excitation wavelength range, in contrast to the behaviour observed in resorcinol.

4.2 Origins of τ_2

In contrast to τ_1, the origins of τ_2 are more difficult to assign. We first look to collate the evidence involving τ_2 and then attempt to resolve its origins. From the [resorcinol-d_2]$^+$ TR-IY transients it can be seen that, following deuteration, τ_2 is no longer an accessible pathway. This therefore implies that the process responsible for τ_2 is likely to be barriered in some way since deuteration will greatly reduce the probability of tunnelling through this barrier. This proposal is also supported by the extracted lifetimes for τ_2 (see Figure 3(d-e)), which are typical of a non-ballistic (non-ultrafast) process. It should also be noted that, while the resorcinol$^+$ transient collected at 255 nm probe wavelength displays mono- rather than a bi-exponential character, the time constant extracted at this wavelength is similar to the values for τ_2 extracted at 264 and 260 nm. As such, it is very difficult to ascertain whether there is truly only a single relaxation process being probed at 255 nm or if two processes of a similar rate are occurring simultaneously.

From the above arguments, several conclusions can be drawn. First of all, as a single exponential fit alone is necessary for all τ_H which correlates with τ_1, it is unlikely that the mechanism that results in τ_2

is in direct competition with H atom tunnelling / IC. This would make IVR seem the most straightforward explanation. However the timescales involved cast doubt over this conclusion. IVR generally onsets when the density of states accessed is ~100 per cm^{-1} [75], which, from our DOS calculations, occurs in resorcinol at ~800 cm^{-1} excess energy. Above this threshold, the rate of IVR is expected to increase with increasing energy, following a similar density of states argument as presented for IC above. This limit is greatly exceeded at the energies at which τ_2 onsets. Given that our observed timescales are on the order of tens to hundreds of ps and that this time component activates ~1900 cm^{-1} above the $1^1\pi\pi^*$ origin, it is unlikely that such an IVR process is responsible for the bi-exponential decay observed here. In addition, whilst we concede that timescales for IVR on the order of a hundred picoseconds have been observed in benzene previously,[76] the enhanced DOS through additional functional groups in resorcinol will likely result in an increased rate of IVR.

We can also rule out a mechanism associated with a prefulvenic CI within resorcinol. Prefulvenic CIs in phenol are known to exist ~6400 cm^{-1} above the $1^1\pi\pi^*$ origin[31] and, given the similarities between phenol and resorcinol, it is reasonable to assume the prefulvenic CIs will reside in approximately the same energetic location (see Fig. 2(d)). Taking this assumption into account, it is unlikely that prefulvenic CIs are responsible for τ_2, as the onset occurs at $\geq$264 nm (~1900 cm^{-1} excess energy).

Given that the deuterated data show no τ_2 component, any alternative suggestions must point towards a barriered process. Armed with this knowledge, we provide two suggestions for the origins of τ_2:

(1) A keto-enol tautomerisation (KET) mechanism, involving either one or both OH groups. Such a process would likely need to overcome, or tunnel through a barrier before tautomerisation could occur.[77, 78] Previous experiments have placed the vibrational modes that would likely mediate the KET mechanism, which include the O-H bend, at ~1300 cm^{-1} in the ground state of resorcinol.[33, 35] A similar

excess energy would be expected for the O-H bend in the $1^1\pi\pi^*$ excited state which is in fairly good agreement with the onset of τ_2 (>1900 cm^{-1}). To verify this proposed mechanism, appropriate methylation at carbon positions adjacent to C-OH, would prevent KET. Assuming that methylation does not influence the electronic structure significantly, this may assist in validating such a KET mechanism.

(2) The second explanation derives from consideration that conformer C (inset Figure 1) may be participating in the excited state dynamics. While conformer C has not been spectroscopically observed in previous experiments, τ_2 is observed when exciting with sufficient energy (>1900 cm^{-1}) for conformer A or B to potentially overcome the torsional barrier for interconversion from conformer A or B into C. Our calculations have indeed shown that the torsional barrier in switching between various conformers in the $1^1\pi\pi^*$ state corresponds to ~2100 cm^{-1}, in very good agreement with this experimental onset. Once in conformer C, relaxation involving a barriered pathway may explain how deuteration effectively switches off conformer C-driven dynamics resulting in τ_2, as evidenced by our results presented in Figure 3.

We end this section by considering the role of conformer specific dynamics further. As noted above, calculations for tunnelling probabilities were performed based on the PECs yielding tunnelling probabilities of 1.2×10^{-3}, 1.9×10^{-5} and 2.1×10^{-4} for H-atom tunnelling along the O^1-H, O^2-H and O^3-H coordinates, respectively. Based on this simplified approach, one would anticipate that τ_H is attributed primarily to H-atom tunnelling in conformer A along the O^1-H coordinate. This presents us with the tantalising prospect of demonstrating conformer specific tunnelling dynamics. To validate this conundrum, high resolution H(Rydberg) atom photofragment translational spectroscopy measurements (such as those described in detail in reference 28) could potentially enable one to glean information on whether tunnelling mediated dynamics in resorcinol is indeed conformer specific. Similarly, a more expansive theoretical approach would be required to assess the potential role of conformer specific

tunnelling. In the first instance, PECs wherein the geometry is relaxed at each point along O-H would certainly be advantageous, although fully multi-dimensional potential energy surfaces would invariably enable us to learn more information regarding this and the tunneling arguments, involving interconversion between conformers, put forth in the preceding paragraphs.

5. Conclusions

The excited state dynamics of resorcinol following UV excitation at a range of pump wavelengths, 278 – 255 nm, have been investigated using a combination of ultrafast time-resolved ion yield measurements and time-resolved velocity map ion imaging coupled with complementary *ab initio* calculations.

Following excitation to the $1^1\pi\pi*$ state below the $1^1\pi\pi*/^1\pi\sigma*$ CI, we extract a timescale for excited state relaxation, τ_1, that decreases as a function of excitation energy from 2.70 ns to ~120 ps. This is ascribed to a competition between two relaxation mechanisms; H atom tunnelling beneath the CI, followed by coupling onto the dissociative $^1\pi\sigma*$ state, yielding H atoms with high KE (~5000 cm^{-1}); and an IVR driven IC process that is able to transfer population from the photoexcited $1^1\pi\pi*$ state back to a vibrationally excited ground state, S_0*. We assign the increase in the rate of decay of the $1^1\pi\pi*$ state to an enhancement in the density of vibrational states with increasing pump energy, leading to a more efficient IVR process in out-of-plane modes which can promote IC onto S_0*, eventually resulting in IC becoming the kinetically dominant decay pathway, with complete depopulation of the $1^1\pi\pi*$ state occurring in ~120 ps following excitation at 255 nm.

When exciting between 264 – 260 nm a bi-exponential decay is observed in the TR-IY transients. This time constant, τ_2, is still somewhat difficult to interpret. At this time we put forth two possible explanations as to the origins of τ_2; keto-enol tautomerisation or conformer specific dynamics. The deuterated results (τ_D) show no evidence of τ_2, suggesting that this process is barriered in some way. To confirm the validity of these explanations, however, requires further experimental and theoretical

work, which we suggest may be the focus of a follow-up paper.

Excitation above the $1^1\pi\pi^*/^1\pi\sigma^*$ CI yields H atoms produced on an ultrafast timescale as observed in previous investigations.[27, 29] Following UV excitation with 237 nm light, high KE H atoms (~11000 cm^{-1}) are produced in ~260 fs in line with a mechanism involving direct dissociation from the $^1\pi\sigma^*$ state or ultrafast coupling between the $1^1\pi\pi^*$ (or $2^1\pi\pi^*$) and $^1\pi\sigma^*$ state followed by dissociation.

The results presented above continue to provide insight into the deactivation processes that are prevalent in systems possessing a purely dissociative state. When compared to previous experiments, these results highlight the profound effect the presence of additional functional groups, and more specifically the precise location of the functional groups, can have on the excited state dynamics of model heteroaromatic systems following UV excitation.

Notes and references

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Table 1. Calculated vertical excitation energies (ΔE_{vert}) and oscillator strengths (*f*) for resorcinol at the TD-PBE0/aug-cc-pVTZ, EOM-CCSD/aug-cc-pVDZ and CASPT2/aug-cc-pVTZ. Bond dissociation energies (BDE), D_0, calculated at the PBE0/aug-cc-pVTZ level are also provided. The experimental value for the first excited state of conformers A and B is also presented for comparison. O^x-H labels from Figure 1.

	ΔE_{vert}/eV (*f*)		Conf. A	
State	**TD-PBE0**	**EOM-CCSD**	**CASPT2**	**Expt[a]**
$1^1\pi\pi^*$	5.08 (0.0339)	4.99 (0.0255)	4.45	4.46
$1^1\pi\sigma^*$	5.23 (0.0004)	5.43 (0.0003)	5.46	
$2^1\pi\sigma^*$	5.48 (0.0000)	5.72 (0.0001)	--	
$2^1\pi\pi^*$	5.81 (0.0091)	6.12 (0.0200)	5.64	

	ΔE_{vert}/eV (*f*)		Conf. B	
State	**TD-PBE0**	**EOM-CCSD**	**CASPT2**	**Expt[a]**
$1^1\pi\pi^*$	5.11 (0.0252)	4.99 (0.0179)	4.43	4.49
$1^1\pi\sigma^*$	5.23 (0.0000)	5.41 (0.0000)	5.50	
$2^1\pi\sigma^*$	5.49 (0.0011)	5.70 (0.0006)		
$2^1\pi\pi^*$	5.78 (0.0068)	6.08 (0.0202)		

BDE/cm^{-1}	
Co-ord	**PBE0**
O^1-H	28930
O^2-H	29340
O^3-H	29360

[a]Ref. 36.

Figure 1. Vapour-phase absorption spectrum of resorcinol between 300 – 210 nm, indicating the excitation wavelength range ($h\nu_{pu}$) investigated in this study. Molecular structures of the three conformers (A, B and C) are shown inset.

Figure 2. (a) Calculated 1-D potential energy cuts of the S_0, $1^1\pi\pi^*$ and $1^1\pi\sigma^*$ electronic states along the O^1-H (black circles), O^2-H (blue circles) and O^3-H (red circles) bond dissociation coordinates ($R_{On\text{-}H}$) in resorcinol. Cuts are calculated at the CASPT2(12,10)/aug-cc-pVTZ level. Shaded areas indicate the excitation regions for the range 278 nm – 255 nm (purple) and 237 nm (green). Also included is the $2^1\pi\pi^*$ (grey squares) which is based upon the calculated profile for the $1^1\pi\pi^*$ and corrected to the CASPT2 vertical excitation energy value for conformer A (see Table 1). Inset: Tunnelling probabilities for the three O^n-H coordinates as calculated using the WKB method. Right are shown calculated gradient difference (GD) and derivative coupling (DC) branching space motions associated with the CI geometries for the minimum energy crossing points between (b) $1^1\pi\pi^*/^1\pi\sigma^*_{O1\text{-}H}$, (c) $^1\pi\sigma^*_{O1\text{-}H}/S_0$, (d) $1^1\pi\pi^*/S_0$ and (e) $2^1\pi\pi^*/1^1\pi\pi^*$.

Figure 3. (a)-(f) Parent ion (resorcinol$^+$) and (g)-(l) deuterated parent ion ([resorcinol-d_2]$^+$) signal transients. Transients were recorded using (1 + 1′) REMPI following excitation at a range of pump wavelengths between 278 – 255 nm and probing at 243.1 nm. Solid lines correspond to kinetic fits. In (d) and (e), dashed red and black lines show components of bi-exponential fits. Extracted timescales are displayed next to the relevant parent ion trace.

Figure 4. H atom TKER spectra collected over a pump wavelength range of 278 – 255 nm, (a)-(f) respectively. Vertical black arrows indicate the predicted $TKER_{max}$ for $^1\pi\sigma^*$ mediated dynamics. Inset: Example H^+ velocity map image from which the TKER spectra are derived (left half) together with a reconstructed slice through the centre of the original 1D ion distribution (right half). The vertical white arrow indicates the electric field polarisation of the pump pulse, ε. Spectrum (a) has been fit to a Boltzmann background signal (green solid line) and a Gaussian peak (black solid line) corresponding to resorcinoxyl radical production.

Figure 5. Normalised H^+ signal transients for the high TKER (Gaussian) feature at each pump wavelength obtained by integrating the signal between 3000–8000 cm^{-1} in TKER spectra recorded at many Δt. A kinetic fit to the trace is shown by the solid red line with extracted time constant (τ_H) displayed beneath. For panels (a) and (b), the transients are fit with the time constant extracted from the resorcinol$^+$ transient (τ_1, dashed blue line), see text for more details.

Figure 6. (a) H atom TKER spectrum obtained following excitation at 237 nm, showing a peak at ~11000 cm^{-1} corresponding to production of X state resorcinoxyl radicals (shaded green) and one at ~4000 cm^{-1} corresponding to A state radical production (shaded blue). Predicted $TKER_{max}$ values for dissociation into the X and A state product channels are shown by the vertical black and red arrows, respectively. Inset: H^+ velocity map image from which the TKER spectrum is derived (left half) together with a reconstructed slice through the centre of the original 1D ion distribution (right half). (b) H^+ signal transient following excitation with 237 nm light (circles), obtained by integrating the signal between 8000–14000 cm^{-1} in TKER spectra recorded at various Δt. An overall kinetic fit to the trace is shown by the solid green line with the extracted time constant (τ_4) below.

Figure 7. Calculated density of vibrational states in the $1^1\pi\pi^*$ state of resorcinol for conformers A (blue line) and B (red line), and phenol (grey dashed line), along with measured rates of decay of the $1^1\pi\pi^*$ state, k_1 (blue circles) and k_2 (black diamonds) - and of H atom appearance, k_H (red squares) – in resorcinol, plotted as a function of excess vibrational energy in the $1^1\pi\pi^*$ state, E_{vib}.

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