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Time-resolved photoelectron imaging of excited state relaxation dynamics in phenol, catechol, resorcinol and hydroquinone

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Time-resolved photoelectron imaging of excited state relaxation dynamics in phenol, catechol, resorcinol, and hydroquinone

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Time-resolved photoelectron imaging was used to investigate the dynamical evolution of the initially prepared S_1 ($\pi\pi^*$) excited state of phenol (hydroxybenzene), catechol (1,2-dihydroxybenzene), resorcinol (1,3-dihydroxybenzene), and hydroquinone (1,4-dihydroxybenzene) following excitation at 267 nm. Our analysis was supported by *ab initio* calculations at the coupled-cluster and CASSCF levels of theory. In all cases, we observe rapid (<1 ps) intramolecular vibrational redistribution on the S_1 potential surface. In catechol, the overall S_1 state lifetime was observed to be 12.1 ps, which is 1–2 orders of magnitude shorter than in the other three molecules studied. This may be attributed to differences in the H atom tunnelling rate under the barrier formed by a conical intersection between the S_1 state and the close lying S_2 ($\pi\sigma^*$) state, which is dissociative along the O–H stretching coordinate. Further evidence of this S_1/S_2 interaction is also seen in the time-dependent anisotropy of the photoelectron angular distributions we have observed. Our data analysis was assisted by a matrix inversion method for processing photoelectron images that is significantly faster than most other previously reported approaches and is extremely quick and easy to implement. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4765104>]

I. INTRODUCTION

During the past 25 years, the spectroscopy and dynamics of electronically excited phenol (hydroxybenzene) in the gas-phase has received considerable experimental^{1–14} and theoretical^{15–25} attention. Phenol is the chromophore site in several biologically active molecules including the amino acid tyrosine and the estrogenic hormones. This has frequently been cited as a motivating factor for such studies. In particular, the role of the interaction between the optically bright S_1 ($\pi\pi^*$) electronic state and the nearby S_2 ($\pi\sigma^*$) state, which is dissociative along the O–H stretching coordinate, has been the subject of intensive investigation over the past decade. Such states of $\pi\sigma^*$ character are now widely recognised as playing a key role in the relaxation dynamics of many electronically excited species containing OH, NH, and SH groups and a recent review by Ashfold *et al.* (and references therein) provides an excellent starting point for an overview of the extensive number of studies that have been undertaken in this area.²⁶ The S_2 ($\pi\sigma^*$) state in phenol has been identified as having significant Rydberg (3s) character in the vertical Franck-Condon region. At more extended O–H distances the electron density evolves towards being localised on the OH group and exhibits a node along the O–H bond.¹⁹ The $S_2 \leftarrow S_0$ transition possesses little or no oscillator strength, although it may, in some instances, be accessed directly as a result of vibronic coupling. In addition, radiationless transfer to (and subsequently from) the S_2 state may also take place at conical intersections

(CIs) formed with other electronic states, providing significant mechanistic pathways for electronic relaxation.

Since 2006, the excited state dynamics of phenol (and some of its substituted derivatives) have been comprehensively investigated by Ashfold and co-workers, leading to significant new photophysical insight.^{27–34} Using H Rydberg atom photofragment translational spectroscopy (HRA-PTS), this group have identified two different photodissociation mechanisms following excitation at wavelengths longer or shorter than 248 nm. At the S_1 origin (275.11 nm) the H atom kinetic energy release distribution is bimodal, exhibiting an unstructured “slow” component and a “fast” component comprising a series of structured peaks that are correlated with the formation of specific vibrational levels in the ground electronic state of the \tilde{X}^2B_1 phenoxyl radical co-fragment. Both of these components show an isotropic recoil distribution. As the excitation wavelength is gradually shortened, similar H atom distributions are observed, although the resolution in the fast component gradually decreases, becoming completely unresolved at around 257 nm. The origin of the fast component has been the subject of some conjecture, and a pathway involving $S_1 \rightsquigarrow S_0^\# \rightsquigarrow S_2$ non-radiative relaxation (where $S_0^\#$ denotes the electronic ground state with substantial O–H stretching excitation) has previously been proposed.^{1,28} However, the most recent work by the Ashfold group³⁴ now appears to confirm that this feature arises due to H atom tunnelling under the potential barrier formed by a conical intersection (CI) between the S_1 and S_2 surfaces, with subsequent dissociation along the S_2 O–H coordinate. The S_1 and S_2 electronic states of phenol are of different symmetry and, as such,

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should not undergo coupling. However, vibrational modes of specific symmetry may induce a vibronic interaction between the two potential surfaces. Working within the framework of the G_4 symmetry point group (and the Wilson mode labelling scheme³⁵), a detailed analysis of the energy disposal within the phenoxyl co-fragment has provided strong evidence that odd quanta excitation in the ν_{16a} (a_2) ring torsion mode is responsible for mediating the S_1/S_2 interaction.³⁴ This tunnelling interpretation, as previously proposed by Sobolewski *et al.*,¹⁹ also now appears to be supported by additional recent experimental and theoretical work from several groups.^{14,25,36} In particular, recent work from Stavros and co-workers monitoring the time-resolved appearance of H atom photoproducts has concluded that excitation of vibrational modes orthogonal to the O–H stretching coordinate (so-called “spectator modes”) has no significant effect on the H atom tunnelling rate.¹⁴ At excitation wavelengths with insufficient energy to populate $\nu_{OH} = 1$ in the S_1 state (>250 nm), tunnelling therefore always proceeds exclusively from the zero-point energy (ZPE) level of this mode. These authors also reported time-resolved decay traces of the phenol parent ion, observing a fall in the overall S_1 lifetime with increasing excitation energy. It was suggested that this may be due to a competing mechanism involving an $S_1 \rightsquigarrow S_0$ IC pathway driven by the spectator modes.

As the excitation wavelength is reduced below 248 nm, the intensity of the fast H atom signal begins to fade and a new, structured, fast H atom product channel begins to appear in its place. This new channel exhibits significant recoil anisotropy ($\beta \sim -0.5$) and a considerably higher average kinetic energy. This observation has previously been attributed to S_1 excitation above the barrier formed by the S_1/S_2 CI, followed by rapid internal conversion to the S_2 potential surface and subsequent O–H bond fission on a timescale faster than the parent rotational period.²⁸ However, an alternative mechanism invoking direct excitation to the S_2 state (facilitated by ν_{16b} (b_1) mediated vibronic coupling with the higher-lying S_3 ($\pi\pi^*$) state) has recently been proposed.^{25,34}

At all excitation wavelengths between 275 nm and 193 nm, the slow component present in the H atom kinetic energy release distribution has been attributed, in part, to a second non-adiabatic interaction between the S_2 and S_0 potential surfaces at highly extended O–H distances. Subsequent intramolecular vibrational redistribution (IVR) then leads to “statistical” dissociation of the highly vibrationally excited S_0 state, providing a route to excited state \tilde{A}^2B_2 phenoxyl radicals.^{10,11,28} This interpretation is, however, not fully reconciled with time-resolved H atom elimination studies of Stavros and co-workers, who observe both the fast and slow kinetic energy channels to appear on an extremely rapid (<200 fs) timescale following excitation at 200 nm.^{12,13} A second contribution to the slow H atom component is also believed to arise from (unwanted) multiphoton absorption and subsequent decay of “superexcited” states.^{27,37}

In contrast to phenol, the spectroscopy and dynamics of the excited electronic states of gas-phase catechol (1,2-dihydroxybenzene), resorcinol (1,3-dihydroxybenzene), and hydroquinone (1,4-dihydroxybenzene) have received comparatively little attention. UV absorption spectra of all three

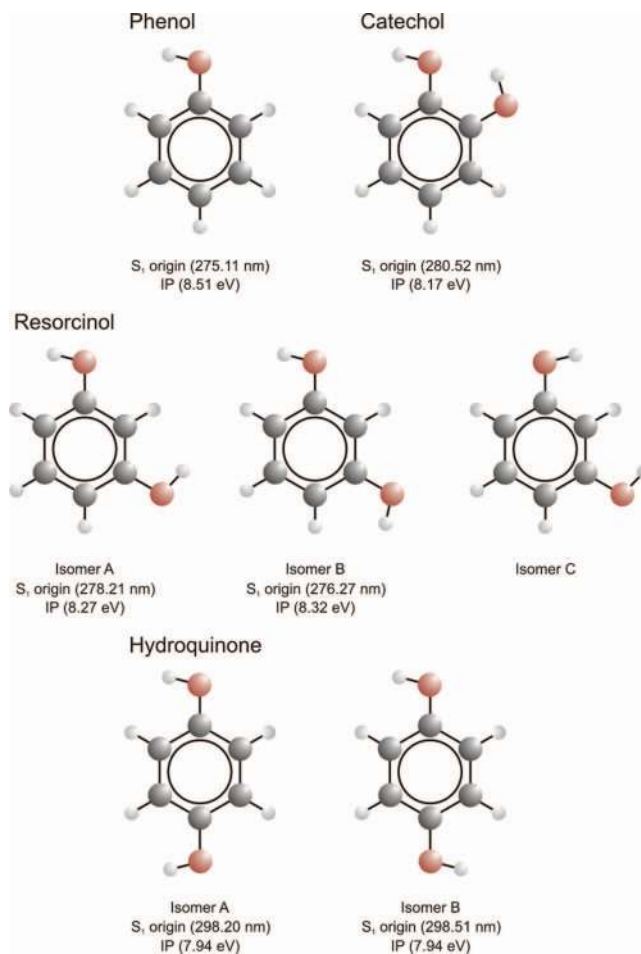


FIG. 1. Schematic depiction of phenol, catechol, resorcinol and hydroquinone. The conformers shown are those that are expected to be present under molecular beam conditions. The positions of the respective S_1 origins are also given along with the adiabatic ionization potentials. Note that isomer C of resorcinol is predicted to exist but has not been observed spectroscopically.

species, recorded in a cell at elevated temperature, were first reported by Beck in 1950.³⁸ More recent work by Lubman and co-workers employed molecular beam methods to record (1+1) resonance enhanced multi-photon ionization (REMPI) spectra of all three molecules – observing well-resolved vibrational structure close to the S_1 origins³⁹ – and a small number of additional spectroscopic studies in the UV have subsequently been performed on the S_1 state in each of the catechol,^{40–43} resorcinol^{44–47} and hydroquinone^{46,48–53} systems. In catechol, a hydrogen bonding interaction between one of the OH groups and the adjacent O atom means that only a single, planar S_0 conformer is present in the gas-phase at room-temperature.^{54–56} In the S_1 state, the free O–H bond lies out of the plane defined by the rest of the molecular framework by $\sim 24^\circ$.⁴² In contrast, both resorcinol and hydroquinone have two planar S_0 conformers that are present even under jet-cooled molecular beam conditions and two different S_1 origins are therefore observed (see Figure 1). As in the case of phenol, the S_1 excited state equilibrium geometries of resorcinol and hydroquinone are also found to be planar.^{44,50}

Very recently, Ashfold and co-workers have reported a detailed study of the S_1 ($\pi\pi^*$)/ S_2 ($\pi\sigma^*$) excited state

electronic dynamics in catechol.⁵⁷ By employing a similar experimental methodology to their previous studies on phenol, this group obtained HRA-PTS data at a range of excitation wavelengths between 280.52 nm (the S_1 origin) and 193.3 nm. In instances when $\lambda > 270$ nm, a bimodal (and isotropic) H atom kinetic energy release distribution with a structured fast component was observed. This was interpreted in a manner similar to phenol, with tunnelling (of the non-hydrogen bonded H atom) under the S_1/S_2 barrier giving rise to the fast component, and analysis of the energy disposal in the catechoxyl radical co-fragment suggesting that this is vibronically mediated by ring-puckering modes. It was also noted that the catechoxyl radical product state distribution was highly sensitive to the degree of OH torsional excitation (of the non-H-bonded group) in the catechol S_1 state. A significant red shift in the energetic position of the catechol S_1/S_2 CI relative to phenol was principally attributed to a reduction of the S_2 vertical excitation energy as a consequence of the large (≥ 2500 cm^{-1}) decrease in O–H bond strength. This decrease arises due to both the electron donating properties of the additional *ortho*-substituted hydroxy group and the intramolecular hydrogen bonding interaction between one of the OH groups and the adjacent O atom. As the excitation wavelength is shortened below 270 nm, a broad but unresolved distribution of fast H atoms gradually evolves to higher average kinetic energy. The emergence of a competing H atom elimination mechanism involving direct excitation to the S_2 state was suggested to account for this observation.

In this present paper, we report our recent investigations of the relaxation dynamics in gas-phase phenol, catechol, resorcinol, and hydroquinone using time-resolved photoelectron imaging following excitation at 267 nm. We see clear differences as well as some strong similarities in the temporal evolution of all four systems, with two clear dynamical timescales being apparent in all cases. Additionally, the information present in the photoelectron angular distributions we observe provides further mechanistic insight. The experimental apparatus we have employed has only recently been developed in our laboratory and we will therefore devote some time to a detailed description of the set-up as well as the methodology employed for data analysis, in addition to the discussion of the data we have obtained. The catechol system is of particular interest as it is a sub-unit of the 5,6-dihydroxyindole molecule, which is known to be an important building block in the eumelanin pigmentation system, the primary role of which is to protect the body from the potentially damaging effects of UV radiation. As such, this study complements our previous time-resolved work on gas-phase indole and 5-hydroxyindole.⁵⁸ Dihydroxybenzenes are also key constituents of many other biomolecules including various flavonoids and the hormones dopamine and adrenaline. Developing a more detailed general understanding of the photochemical behaviour of phenolic systems is therefore of great importance.

II. EXPERIMENTAL

The experiments were conducted using a newly designed and constructed velocity-map photoelectron imaging spec-

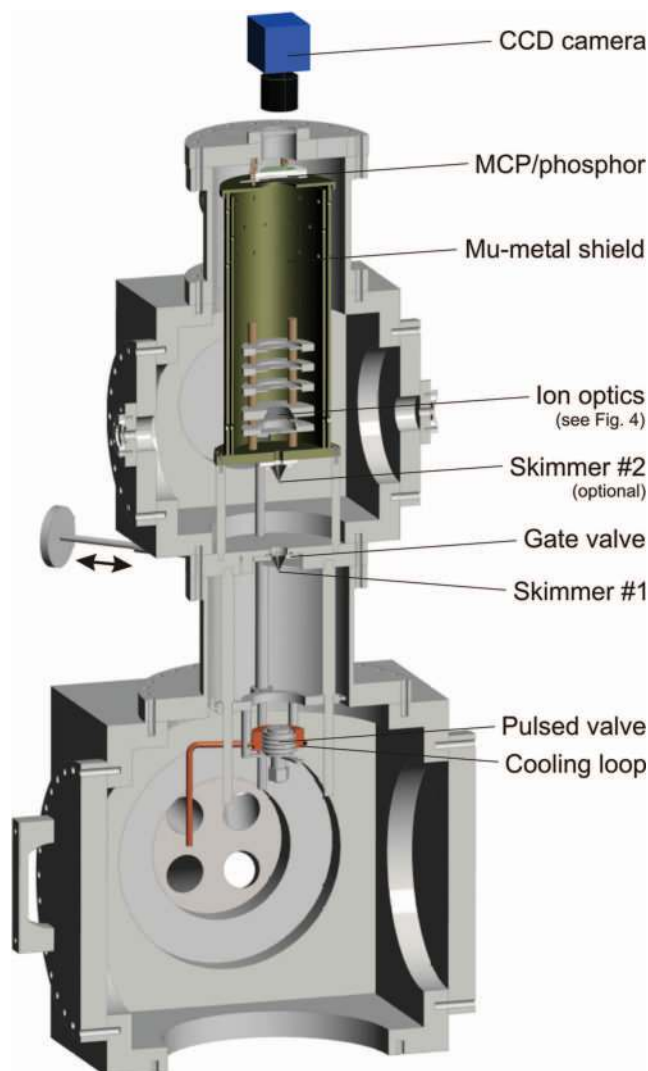


FIG. 2. Cut-through section of the photoelectron imaging spectrometer used in the current experiments. For additional information see the main text. For clarity, some additional details such as vacuum pumps, bake-out lamps and vacuum feedthroughs are omitted. The two mu-metal shielding cylinders have internal diameters of 102 mm and 112 mm and are 2 mm and 3 mm thick, respectively. The mu-metal end-cap and base plate are 3 mm and 5 mm thick, respectively, with the former having a 40 mm central hole.

trometer, which has not previously been described in detail elsewhere. This differentially pumped, ultra-high vacuum apparatus consists of a source chamber and a main interaction chamber, which were evacuated using separate turbomolecular pumps (Edwards Vacuum, 2200 l/s and 480 l/s respectively). An overview of the system is shown in Figure 2. The two chambers were connected by a 1.0 mm skimmer (Beam Dynamics Inc) mounted on a translatable gate-valve assembly⁵⁹ that allowed the source chamber to be vented to atmospheric pressure while the main chamber maintained base vacuum (1×10^{-8} mbar). The advantage of this set-up is that samples mounted within the source chamber (as described in more detail below) could be replenished without the need for a time consuming bake-out of the main chamber before the experiments were restarted. This significantly enhanced the data collection rate, with typical turnaround times for sample replacement and subsequent recommencement of photoelectron acquisition being on the order of just

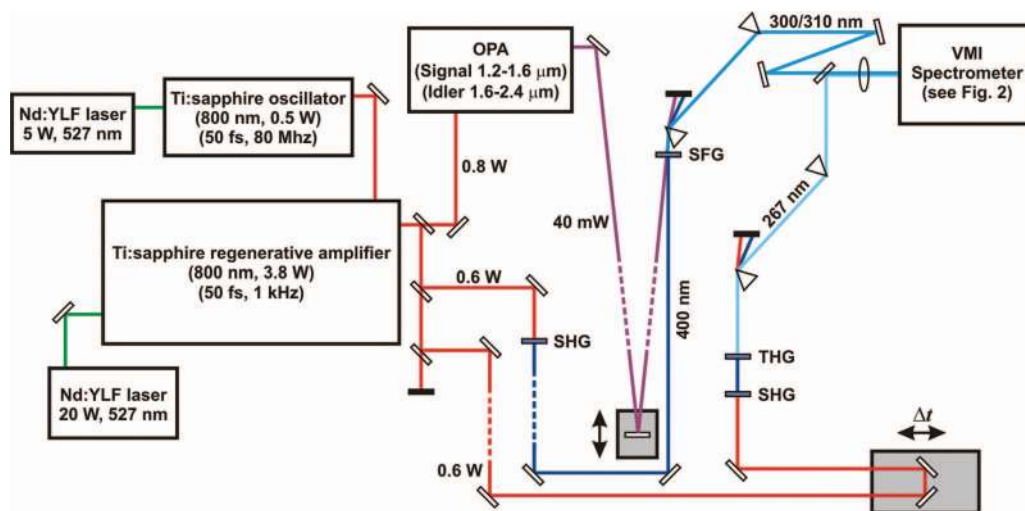


FIG. 3. Schematic overview of the optical set-up used in the current experiments. Telescoping optics (not shown) were used to reduce the size of the 800 nm beams to ~ 5 mm and to ensure that the probe beam focus was smaller than that of the pump. The angle between the 400 nm and OPA signal beams in the sum-frequency generation (SFG) stage is greatly exaggerated.

2 h. Phenol ($\geq 99.5\%$, m.p. 40.5°C), catechol ($\geq 99\%$, m.p. 105°C), resorcinol (99% m.p. 110°C), and hydroquinone (99%, m.p. 172°C) were all purchased from Sigma-Aldrich and used without further purification. These solid samples were brought into the gas-phase using a high intensity, pulsed supersonic molecular beam valve (Even-Lavie, $150\ \mu\text{m}$ diameter conical nozzle).⁶⁰ The three dihydroxy species were held in a cartridge mounted within the valve body (i.e., inside the source chamber), directly behind the exit nozzle. Normal operation of the solenoid driver at 1 kHz raised the temperature of the valve sufficiently to obtain good levels of photoelectron signal without melting the samples, although to regulate this temperature, a copper cooling block was placed over the valve body and connected to a closed-loop chiller unit (Neslab, RTE-110) circulating a 50:50 mixture of ethylene glycol and water. Even with this arrangement, it was not possible to cool the valve sufficiently to prevent samples of phenol from melting and so in this instance, an external gas pick-up cell was used instead. The relatively high vapour pressure of phenol at room temperature (~ 0.45 mbar at 25°C) was sufficient to produce good signal levels. Helium at a pressure of 3 bar was used as a carrier gas in all cases and the samples were translationally and internally cooled via supersonic expansion into the source chamber.

After travelling through the skimmer, which was radiatively heated using a small halogen lamp in order to prevent solid deposition on the tip, the samples passed into the main interaction chamber and were intersected at 90° by co-propagating UV pump and probe pulses. Both pulses were produced from the fundamental output of a regeneratively amplified Ti:Sapphire laser system (Spectra-Physics, Spitfire Pro, 1 kHz, 3.8 W), operating with a 50 fs pulse duration and a central wavelength of 800 nm. Pump energy for the regenerative amplifier was provided by a 20 W Nd:YLF laser (Spectra-Physics, Empower) and the system was seeded by a Ti:Sapphire oscillator (Spectra Physics, Tsunami) pumped by a 5 W Nd:YVO₄ diode-pumped laser (Spectra-Physics, Millennia Pro). The fundamental output was split several

ways on an optical bench, as illustrated schematically in Figure 3, to produce the required UV wavelengths for the experiments. The pump beam (267 nm) was provided by the third harmonic of the Ti:Sapphire output, which was generated using a pair of 0.1 mm BBO crystals. Material dispersion compensation was achieved using a pair of CaF₂ Brewster angle prisms in a single-pass geometry. The probe beam (300 nm or 310 nm in the case of hydroquinone) was generated by sum-frequency mixing the 400 nm second harmonic of the Ti:Sapphire output with the signal beam output (1200 nm or 1375 nm) from an optical parametric amplifier (Spectra Physics, OPA-800C) in a 0.1 mm BBO crystal. Probe wavelengths were chosen to ensure that no absorption to the S₁ state would take place. This ensured the experiments were as “clean” as possible by eliminating the possibility of any significant “probe-pump” dynamics appearing in the photoelectron spectra close to zero delay times. For dispersion management of this beam line, a pair of fused silica Brewster angle prisms were used, also in a single-pass geometry. The temporal delay between the pump and the probe was precisely controlled using a motorized linear translation stage (Physik Instrumente, M-403.62S) and controller (Physik Instrumente, Mercury Step) running under PC command routines for data acquisition developed in-house using MATLAB (The MathWorks Inc, version 7.4.0, 2007a). The pump ($0.5\ \mu\text{J}/\text{pulse}$) and probe ($1.5\ \mu\text{J}/\text{pulse}$) were combined on a thin dichroic mirror and focussed into the spectrometer through a 2.0 mm thick CaF₂ window using a 30 cm fused silica lens.

The interaction between the UV light pulses and the molecular beam containing the sample took place between the repeller and extractor electrodes of an electrostatic lens set-up that was optimised for velocity-map imaging⁶¹ of the photoelectrons produced following (1+1') ionisation by the pump and probe. The design of this lens assembly was modelled using the SIMION software package (Scientific Instrument Services, Version 7.0) and is detailed in Figure 4. One key feature of this set-up is the use of a conical extractor electrode, which gives improved velocity mapping of charged particles

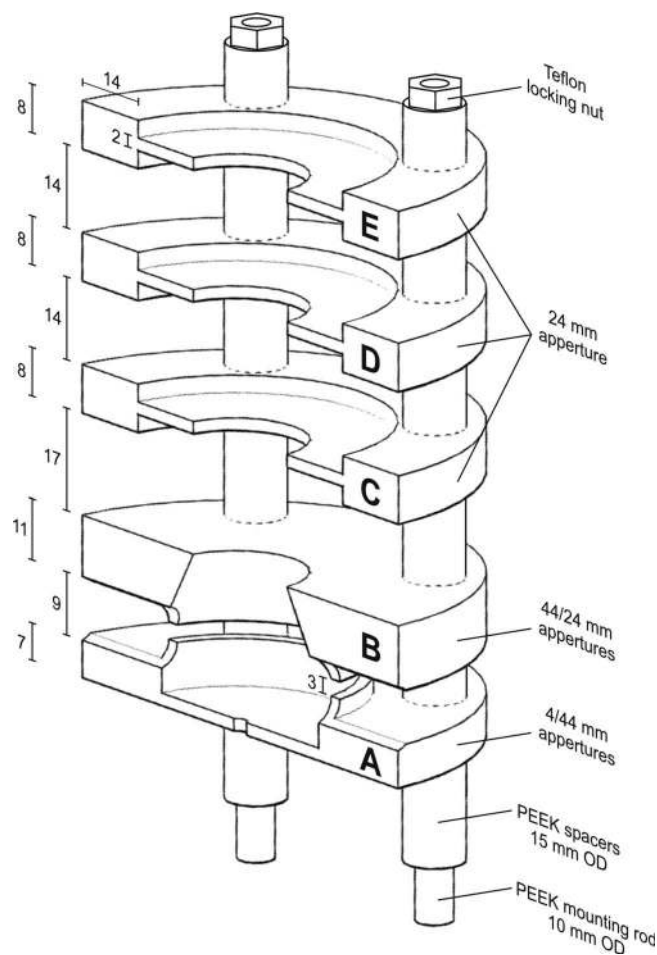


FIG. 4. Detailed cut-through section of the imaging electrode set-up used in the current experiments. All units are shown in mm. Optimum velocity-mapping (for an overall distance of 26 cm between the laser interaction region and the MCP detector) was achieved when the ratio of the voltages applied to the repeller (A) and extractor (B) electrodes was $V_B/V_A \sim 0.78$. The thick outer edge design of all electrodes was to enable mounting of electrical contacts without potentially distorting the field lines along the time-of-flight axis. The overall diameter of all lens elements is 80 mm.

ejected off-axis along the time-of-flight path to the detector when compared to flat, parallel electrode geometries (effectively reducing coma type lens aberration effects). A second key feature of the electrode design is the use of an extruded “lip” on both the repeller and extractor (see Figure 4). This creates a potential barrier close to the edge of these lens elements that effectively screens the insulating components between them from electrons formed in the laser interaction region (eliminating the possibility of point-charge build up and associated field distortions). Similar design features have also previously been employed by other groups.^{62–64} The additional electrodes (D-E) shown in Figure 4 were not required in the current experiments (and were therefore grounded, along with electrode C) but offer the instrument the capability of performing “dc slice imaging” experiments⁶⁵ when running in ion-detection mode.

The VMI electrode assembly and photoelectron flight tube were fully insulated from the effects of stray magnetic fields by a double layer of mu-metal shielding along the time-of-flight axis. A series of small (5 mm) holes around the

top end of these shielding cylinders ensured adequate gas pumping in the region close to the MCP detector. Additional mu-metal shielding was also incorporated into the base plate on which the ion-optics were mounted and an “end-cap” in front of the MCP detector assembly. In order to minimize the effects of stray electric fields within the instrument, all shielding surfaces that could potentially be exposed to photoelectrons were sprayed with colloidal graphite (Acheson Colloids, Aerodag G). The entire main chamber could also be baked to a temperature in excess of 150 °C using small, internally mounted halogen lamps positioned outside the mu-metal shield. A 40 mm dual MCP detector backed by a P47 phosphor screen (Photonis, APD 2 PS 40/12/10/12 I 46:1 P47) was positioned at the end of the photoelectron flight tube. This was mounted in-house onto a custom made flange with a central CF40 viewport, with the overall distance between the interaction region and the detector being 26 cm. The applied voltage on the back plate of the MCP assembly was gated using a high voltage pulser (DEI, PVX-4140). The timing for the MCP gate, as well as for the firing of the pulsed molecular beam valve, was initiated by a multi-channel delay generator (Stanford, DG535), triggered by the software controlling the laser system. Photoelectrons impacting on the MCP/phosphor screen assembly were imaged using a monochrome Firewire CCD camera (The Imaging Source, DMK 21BF04) with a 640 × 480 pixel array. Data was passed from the camera to the PC running the acquisition software at 30 frames per second. We estimate that typical photoelectron acquisition rates were on the order of 5–10 per laser shot, depending on the specific sample. No additional processing of the raw images (such as ion-counting⁶⁶ or centroiding⁶⁷) was performed prior to the full analysis of the data, which will be expanded upon later.

By systematically adjusting the length of the prism compressor in each beam line, a pump-probe cross correlation of 160 ± 15 fs was obtained. This measurement was recorded directly inside the spectrometer from non-resonant, two-colour ($1 + 1'$) multiphoton ionisation of pyrrole. Time-of-flight to energy calibration of the instrument was obtained from three-photon, non-resonant ionisation of xenon and the central wavelengths of both the pump and probe beams were accurately monitored using a USB grating spectrometer (Ocean Optics, USB2000+). A typical data collection run consisted of scanning the translation stage repeatedly between pump-probe delays of -400 fs to $+750$ fs in 50 fs increments and 20 exponentially increasing steps between $+750$ fs and $+100$ ps. At each delay position, pump-probe photoelectron images were recorded for around 10 s, along with images of the time-invariant one-colour pump alone and probe alone signals (for subsequent background subtraction). This was achieved using shutters (Thorlabs, SH05) and controllers (Thorlabs, TSC001) running under the command of the data acquisition software. The experiment was therefore fully automated; permitting typical data accumulation runs of approximately 80–100 scans that lasted for up to 15 h. Temporal drifting of the delay stage was always less than 50 fs during this time period. Spatial overlap between the pump and probe beams was generally very stable over the extended timescale of the experiments, although specific individual scans (or

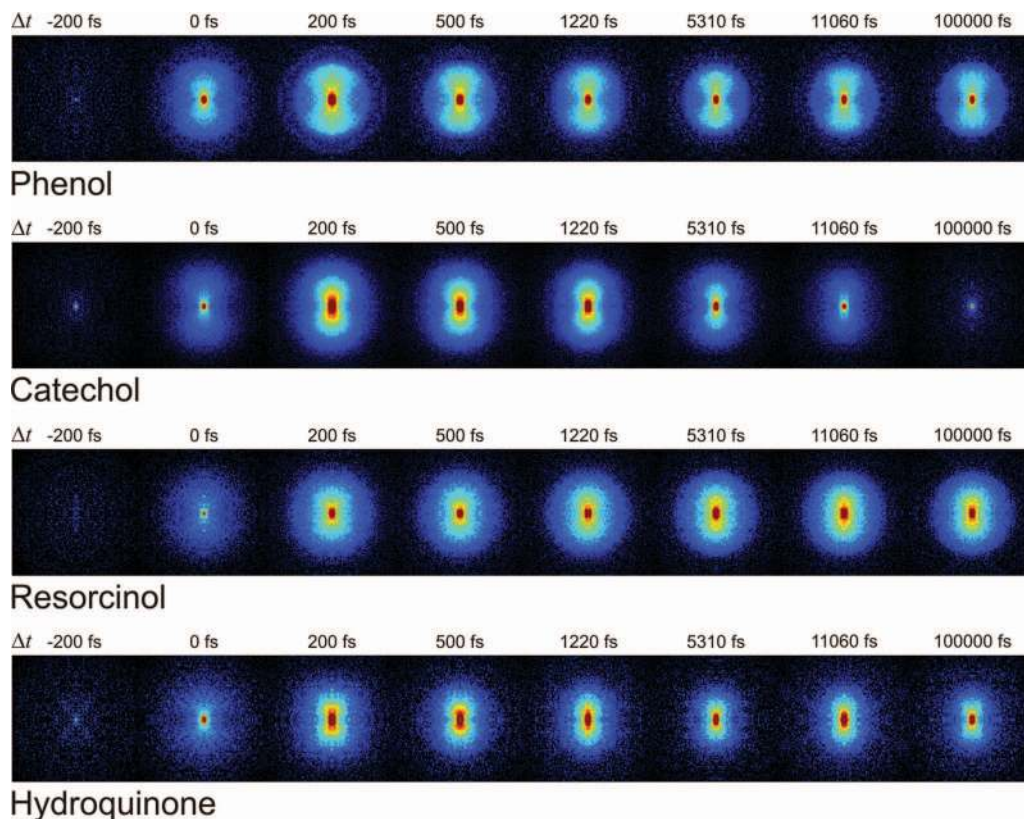


FIG. 5. $(1 + 1')$ photoelectron images recorded at a series of selected pump-probe time delays Δt for the 4 molecules investigated in the present study. Pump-alone (267 nm) and probe-alone (300 nm, 310 nm in the case of hydroquinone) signals have been subtracted and the images are 4-fold symmetrised. The linear polarization direction of both the pump and probe beams is vertical with respect to the images. The seemingly unusual choice of some Δt values is a consequence of the exponential, rather than linear stepping of the delay stage beyond 750 fs. Note that the phenol data was recorded with a lower extractor voltage setting than the other three systems (-1000 V vs. -1500 V) and so a direct size comparison is not meaningful.

groups of scans) could be rejected during the initial data processing stage in instances where the pump-probe signal was lost. Photoelectron image data from all other scans, recorded at each specific pump-probe delay, were then added together for subsequent processing and analysis. In order to assist in the image processing step we employed a matrix inversion scheme that represents a significant speed improvement over many other techniques that have been proposed previously. Our approach is also extremely quick and easy to implement. A full discussion of this treatment may be found in the Appendix.

III. RESULTS

A. Time-resolved photoelectron spectra

In Figure 5 we present a series of photoelectron images resulting from $(1 + 1')$ ionization of phenol, catechol, resorcinol and hydroquinone at a range of selected pump-probe delay times, Δt . These data were generated by subtracting one-colour pump-alone and probe-alone background images from the raw pump-probe image. Using the matrix inversion procedure outlined in the Appendix, along with appropriate time-of-flight to energy calibration information, photoelectron spectra were generated from the full set of 44 background-subtracted images recorded for each system under study. An example of a matrix-inverted image (from

phenol) is presented in Figure 6, and Figure 7 displays the time-resolved spectra obtained for all 4 molecules that were investigated. For clear display of the short-time dynamics, the spectra are plotted on a linear/logarithmic time axis. The energy axis is plotted in terms of electron binding energy as the adiabatic ionization potentials (IP) of all four molecules have been previously reported using high-resolution techniques.^{42,46,68} The data show no “probe-pump” dynamics evolving to negative time delays due to our choice of probe wavelengths (300/310 nm), as discussed previously, and in all cases only the D_0 (π^{-1}) cation electronic state is energetically accessible.^{69,70} All data sets display some short-time (i.e., < 1 ps) dynamics in addition to a longer lived component, although there is a striking difference in the long-time decay exhibited by catechol when compared to phenol, resorcinol and hydroquinone, with the former being considerably faster. In contrast to the other systems under study, the resorcinol data shows a long-time signal that is clearly increasing towards extended pump-probe delays. The phenol spectrum also appears to show some partially resolved (although unassignable) structure at small Δt values. Finally, the photoelectron angular distributions (PADs) seen in all four molecules exhibit considerable anisotropy at all delay times, peaking along the laser polarization axis – a feature we will return to consider later.

The time-dependence of the photoelectron data was analysed using a standard Levenberg-Marquardt global fitting

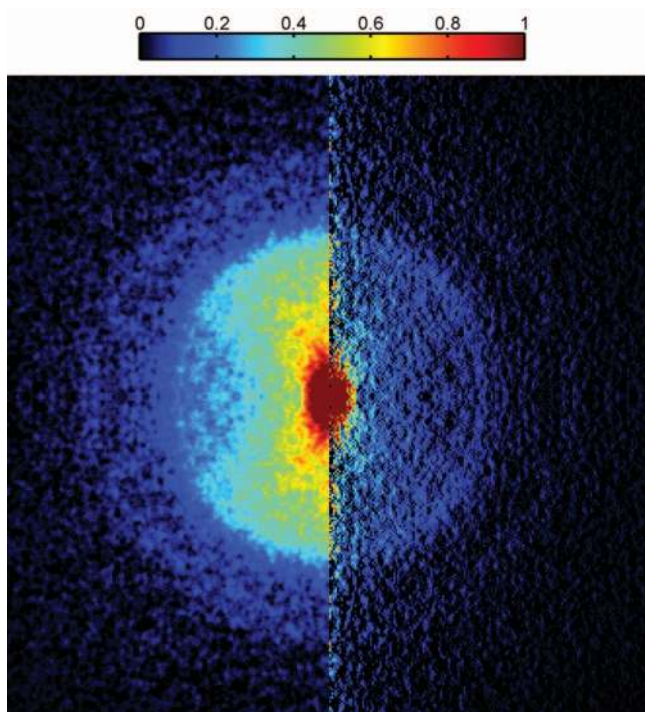


FIG. 6. Left half: Background-subtracted pump-probe photoelectron image from phenol recorded at $\Delta t = 200$ fs. Right half: Same image after Abel inversion performed with the matrix method detailed in the Appendix. The linear polarization direction of both the pump and probe beams is vertical with respect to the image, which was 4-fold symmetrised prior to inversion.

routine wherein the 2D data $S(E, \Delta t)$ are expressed as⁷¹

$$S(E, \Delta t) = \sum_i A_i(E) \cdot P_i(\Delta t) \otimes g(\Delta t). \quad (1)$$

Here $A_i(E)$ is the decay associated photoelectron spectrum of the i th data channel, which has a time dependent population $P_i(\Delta t)$ described by a series of exponentially decaying functions (all of which originate from zero pump-probe delay) and $g(\Delta t)$ is the experimentally determined Gaussian cross-correlation function. This approach yields a series of decay associated spectra (DAS) that plot the relative amplitude of each component in a given multi-exponential fit as a function of electron binding energy. As a general approach, deconvoluting the data in this way greatly assists in the interpretation of the overall molecular dynamics since different processes, occurring on very similar timescales, may often be spectrally resolved from each other in a given DAS, revealing much more information than the time constants alone. Additionally, by requiring that each exponentially decaying function originates from zero pump-probe delay, the appearance of any negative amplitude features in a given DAS reveals the presence of sequential dynamics: i.e., the negative amplitude associated with a short time constant DAS compensates for the positive amplitude associated with a sequential feature (as described by a second DAS) at pump-probe delays close to zero. This choice of “basis” for extracting dynamical information has the advantage of assuming no *a priori* information about the nature (sequential or otherwise) of the dynamical processes involved when fitting data. A good illustrative example of this

approach may be found in the recent work of Stolow and co-workers.⁷¹

In order to non-trivially fit all data sets shown in Figure 7 using Eq. (1), just two exponential functions were required. Figures 8(a)–8(d) show the various DAS obtained for all molecules under investigation along with the associated time constants (which all have an uncertainty of $\pm 15\%$). To illustrate the good quality of this model, Figures 7(e) and 7(f) show the corresponding fit and associated residuals for resorcinol. In all cases, a fast time constant, $\tau_1 = 320$ –990 fs was obtained along with a longer lived constant τ_2 , which spans a range of values between 12.1 ps (catechol) and 980 ps (phenol). In the case of resorcinol, it was not possible to reliably extract a numerical value for τ_2 (given the range of pump-probe delay times sampled) and we can only quote a lower limit of 1 ns. The resorcinol data also shows a very striking negative amplitude component in the τ_1 DAS. This reveals that at least some of the signal associated with the long-lived decay (as described by the τ_2 DAS) must originate from some form of sequential process (as is also initially suggested by the rising photoelectron signal in the corresponding raw data shown in Figure 7(c)). In all four systems the DAS associated with τ_1 and τ_2 span the same binding energy region (although the relative amplitudes are somewhat different) and no significant signal extends below the adiabatic IP. A previous time-resolved study of phenol reported by Schick and Weber has observed the presence of “superexcited” states (i.e., neutral states lying above the adiabatic ionization potential) that may be populated following two-photon absorption via the S_1 state at 275 nm.³⁷ These authors presented photoelectron spectra, recorded using either a (1 + 1 + 1) or a (1 + 1 + 1') ionization scheme where, in the latter case, the ionizing photon was 413 nm. These spectra show a continuous distribution of ion energies extending from the adiabatic IP all the way up to the three-photon energy cut-off. On the electron binding energy plots shown in Figures 7 and 8 (which are calculated by subtracting photoelectron kinetic energies from the total *two-photon* pump + probe energy), the presence of superexcited states would therefore be apparent in the form of signals extending to binding energies below the adiabatic IP. The fact that almost no photoelectron signals are observed in this region strongly suggests that these states are not a significant factor in any of our data.

B. Photoelectron angular distributions

For the case of a two-photon ionization scheme using linear polarization, the time-dependent PADs we have obtained may be expressed as a function of the electron binding energy E and the pump-probe delay time Δt in terms of the well-known anisotropy parameters β_2 and β_4 ,^{72,73}

$$I(E, \Delta t, \theta) = \frac{\sigma(E, \Delta t)}{4\pi} [1 + \beta_2(E, \Delta t)P_2(\cos \theta) + \beta_4(E, \Delta t)P_4(\cos \theta)]. \quad (2)$$

Here, the $P_n(\cos \theta)$ terms are the n th-order Legendre polynomials and $\sigma(E, \Delta t)$ is the time-dependent electron energy distribution. Performing a fit to our data using Eq. (2)

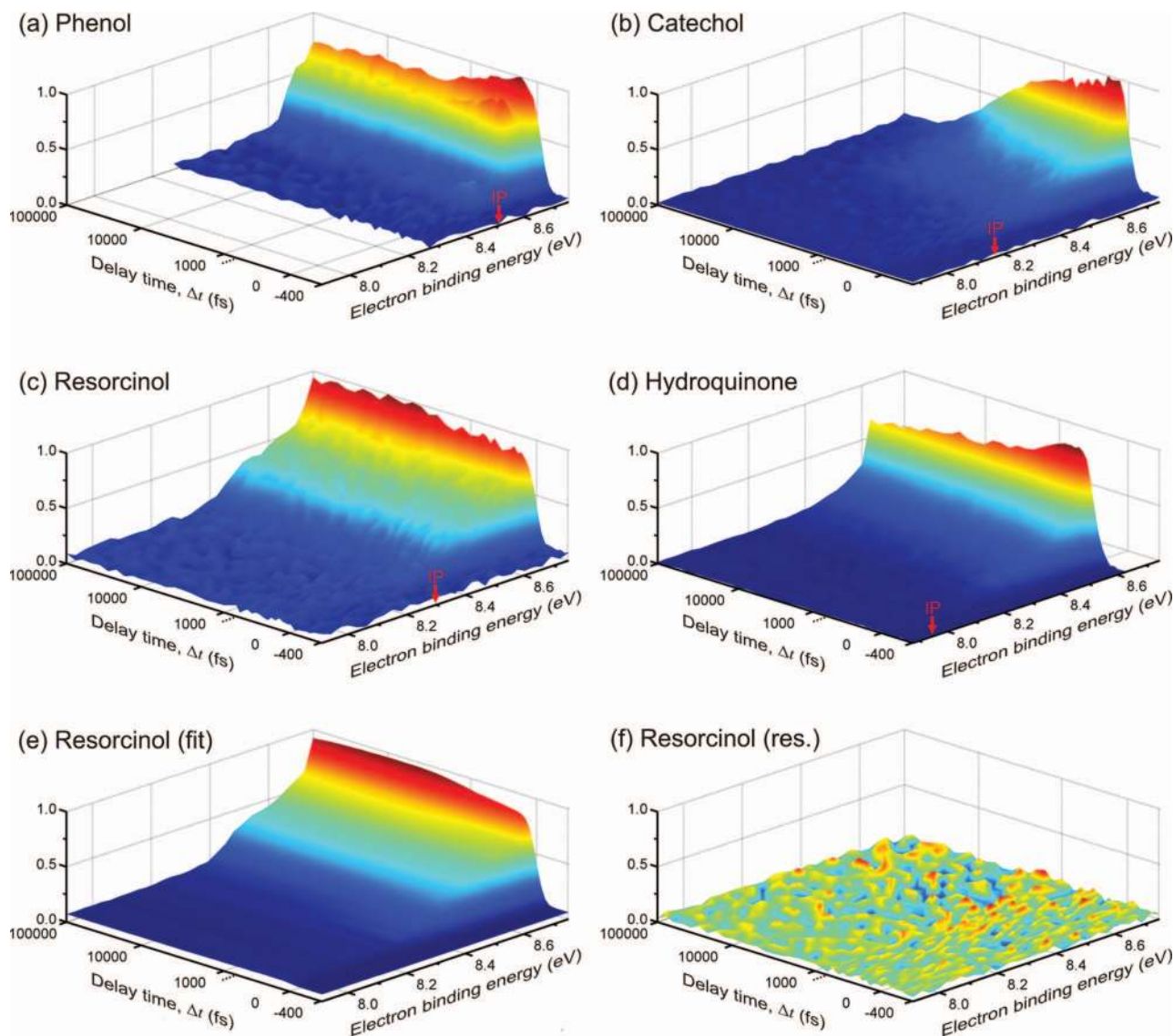


FIG. 7. Time-dependent photoelectron spectra of phenol, catechol, resorcinol, and hydroquinone obtained using a 267 nm pump and a 300 nm probe (310 nm in the case of hydroquinone). The time axis is plotted on a linear scale between -400 fs and $+750$ fs and a logarithmic scale between $+750$ fs and 100 ps. The energy scale is plotted in binding energy based on the following adiabatic ionization potentials: phenol (8.51 eV), catechol (8.17 eV), resorcinol (8.30 eV) and hydroquinone (7.94 eV). These values are marked on the plots. The resorcinol value is an average of those obtained for the A and B isomers shown in Fig. 1. The data is partitioned into 0.03 eV energy bins. Also shown are the fit to the resorcinol data obtained using the procedure described in the main text as well as the associated residuals (i.e., the fit subtracted from the raw data).

reveals that, within statistical uncertainty, β_4 is effectively zero over all regions of the time-dependent photoelectron spectra recorded for all molecules under study. In regions of the photoelectron spectra where only short-time (<1 ps) dynamics are primarily observed, β_2 is also observed to be zero (as is particularly evident, for example, in the isotropic outer ring seen in the phenol image recorded at 200 fs shown in Figure 6), however, in energy regions where longer lived (>10 ps) dynamics are also strongly seen (specific energy regions for each molecule under study are clearly apparent in Figure 8), β_2 is characteristic of a highly anisotropic PAD (as reflected by the inner portion of the image in Figure 6). At any given pump-probe delay time β_2 is largely invariant across this energy region, although there is a clear evolution of β_2 as the pump-probe delay is increased from zero. This evolution

is plotted in Figure 9, which also shows a rising exponential fit to the data. In all four molecules under investigation, β_2 was observed to increase by up to 25%, with the fitted lifetime τ_β ranging from 480 fs (hydroquinone) to 930 fs (resorcinol). Interestingly, in catechol and hydroquinone, the value of τ_β deviates considerably from the value of τ_1 obtained in the DAS fits to the photoelectron data shown in Figure 8. This deviation is too large to simply be attributed to the uncertainty present in the fitted time constants. Even more striking is the fact that in catechol, τ_β is greater than τ_1 (720 fs vs. 320 fs) whereas in hydroquinone this situation is reversed (480 fs vs. 880 fs). This possibly points to a more complex dynamical picture than is suggested by the DAS fits alone and clearly demonstrates the additional insight that the highly differential nature of the photoelectron imaging approach provides.

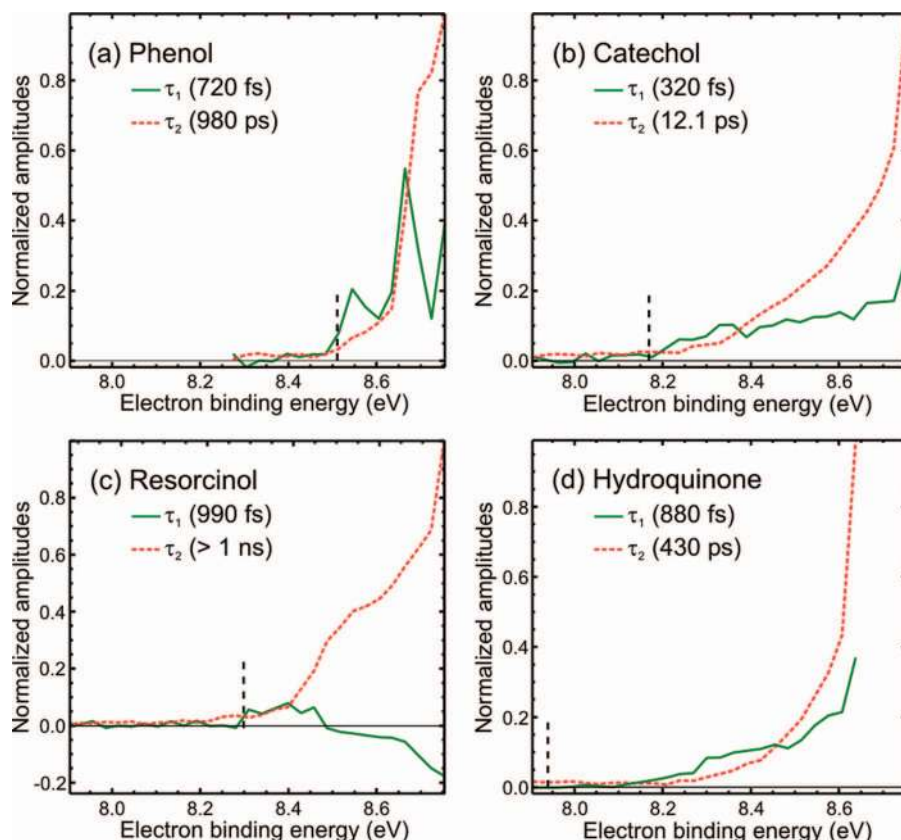


FIG. 8. Decay associated spectra obtained from a global exponential fit to the data presented in Fig. 7. For additional details see the main text. The uncertainty in the values of τ_1 and τ_2 is $\pm 15\%$ in all cases. Vertical dashed lines denote the adiabatic ionization potentials.

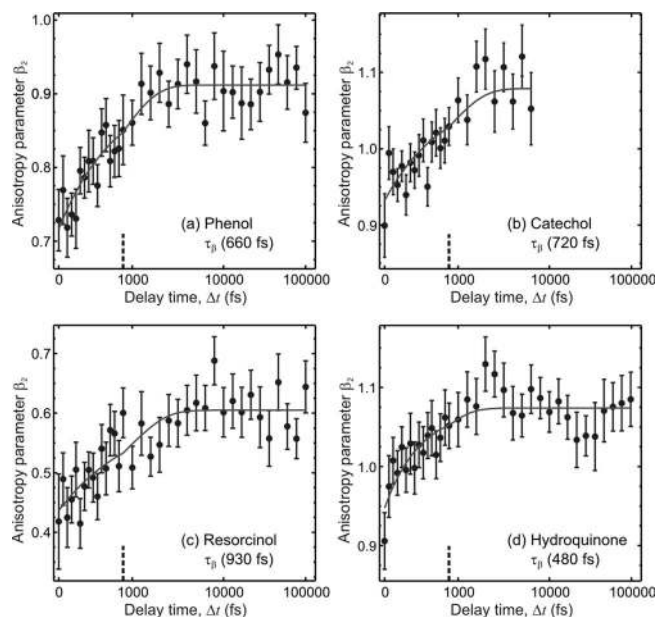


FIG. 9. Fitted values of the anisotropy parameter β_2 as a function of pump-probe delay over energy regions where long-time (>10 ps) dynamics were observed (see Fig. 8). Error bars are one standard deviation. The fits were performed over the angular range $5^\circ \leq \theta \leq 90^\circ$ to eliminate uncertainties from the centre-line noise present in the Abel-inverted images. The solid line is an exponentially rising fit to the data, with associated time-constant τ_β (which has an uncertainty of $\pm 15\%$ in all cases). The time axis is plotted on a linear scale between 0 fs and +750 fs and a logarithmic scale between +750 fs and 100 ps, with the cross-over point denoted by the vertical dashed line.

C. Supporting calculations

The ground state geometries of phenol, catechol, resorcinol, and hydroquinone were optimized using density functional theory (B3LYP) in conjunction with the aug-cc-pVDZ basis set. Vertical excitation energies and oscillator strengths were calculated using equation of motion coupled cluster theory including single and double excitations (EOM-CCSD)⁷⁴ with the aug-cc-pVDZ basis; this is equivalent to linear response (LR) coupled cluster theory for excitation energies. The carbon and oxygen core 1s orbitals were frozen in the correlated calculations. The effect of perturbative triples on the excitation energies were examined for phenol and catechol using the CCR(3) method,⁷⁵ which gives a non-iterative perturbative correction to LR-CCSD excitation energies, such that excitation energies for singly-excited states are correct through third order in the fluctuation potential. It was found that triples affected the excitation by a maximum of 0.15 eV but that, in general, their inclusion had only a negligible effect. The vertical excitation energies and oscillator strengths are presented in Table I. In the case of resorcinol and hydroquinone, values are for the minimum energy isomer (A and B, respectively, as labelled in Figure 1). The oscillator strength of the optically bright $\pi\pi^*$ transition in hydroquinone is almost twice that in the other systems. The $\pi\sigma^*$ state is dark in both phenol and hydroquinone but has a very small oscillator strength for catechol and resorcinol. The S_1/S_2 vertical excitation energy gap in catechol (0.29 eV) is considerably smaller

TABLE I. Calculated EOM-CCSD/aug-cc-pVDZ excitation energies and oscillator strengths. For additional details, see the main text.

	Phenol		Catechol		Resorcinol		Hydroquinone	
	E (eV)	f	E (eV)	f	E (eV)	f	E (eV)	f
$S_1(^1\pi\pi^*)$	4.95	0.046	4.88	0.058	4.90	0.047	4.57	0.107
$S_2(^1\pi\sigma^*)$	5.55	0.000	5.17	0.001	5.41	0.001	5.12	0.000

than in phenol, resorcinol and hydroquinone (which is greater than 0.5 eV in all cases). This may be understood qualitatively in terms of the decrease in O–H bond strength, which is primarily a consequence of the intramolecular hydrogen bonding interaction between one of the OH groups and the adjacent O atom.

Relaxed scans along the O–H dissociation coordinate (valid until before the $S_2(^1\pi\sigma^*)/S_0$ conical intersection) were performed using B3LYP/aug-cc-pVDZ, with those subsequent geometries used to obtain coupled cluster ground (CCSD) and excited state (EOM-CCSD) energies. A similar procedure was used previously in our study of indole and 5-hydroxyindole.⁵⁸ The results are shown in Figure 10. Note that in catechol, the cut is taken along the non-hydrogen bonded O–H coordinate. The resorcinol and hydroquinone cuts are once again for isomer A and isomer B, respectively, and in the case of resorcinol, the dissociation is along the H atom directed away from the other OH group. In all cases our calculations place the bottom of the S_1 state potential-well ~ 0.65 eV too high in energy relative to the position that would be predicted based on the known S_1 origins and O–H zero-point energies. However, such discrepancies are not uncommon in these types of system at the level of theory used and our results are in good agreement with those previously reported for phenol using similar methods (as summarized in Table I of Ref. 34). With respect to the phenol S_1 vertical excitation energy shown in Table I, the differences in the calculated S_1 excitation energies for catechol, resorcinol and hydroquinone agree extremely well with the experimentally observed shifts in the positions of the various S_1 origins.

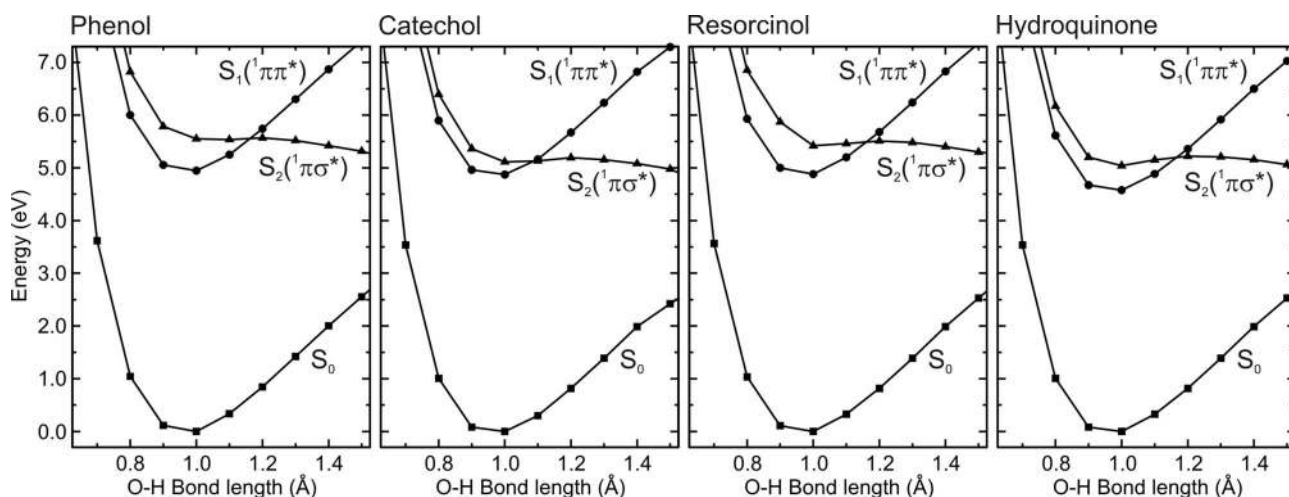


FIG. 10. O–H stretching coordinate potential energy cuts obtained using EOM-CCSD/aug-cc-pVDZ, for phenol, catechol, resorcinol and hydroquinone. For more details see the main text.

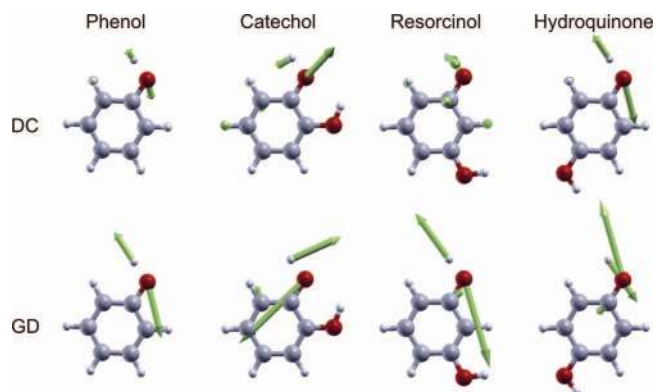


FIG. 11. Branching space vectors for the $S_1(^1\pi\pi^*)/S_2(^1\pi\sigma^*)$ conical intersection (CI) as obtained from CASSCF calculations performed on all four of the molecules used in the present study. The derivative coupling vector (DC) and the gradient difference vectors (GD) define the directions in which the degeneracy is lifted when moving away from the CI point.

Complete-active-space self-consistent-field (CASSCF) calculations were performed to generate qualitatively correct wavefunctions in regions of strong non-adiabatic coupling. Fully relaxed geometry optimisations were performed for the $^1\pi\pi^*$ minimum and the $^1\pi\pi^*/^1\pi\sigma^*$ CI seam. Details of the branching space vectors that lift the degeneracy at the seam minimum are shown in Figure 11 for all 4 molecules. These are seen to involve motion mainly on the dissociating OH bond, with the states coupled through the OH stretch and some out-of-plane bending motion (the extent of which varies across the series). The GAUSSIAN program⁷⁶ was used for the B3LYP, EOM-CCSD, and CASSCF calculations, while the DALTON program⁷⁷ was used for the LR-CCSD and CCR(3) calculations.

In the case of phenol, a recent calculation at the CASPT2(10,10)/aug(O)-AVTZ level of theory³⁴ has proved extremely accurate in predicting the experimentally determined barrier height along the O–H coordinate formed by the S_1/S_2 CI and also in modelling the experimentally observed H atom tunnelling rate under the resulting barrier following excitation to the S_1 origin.¹⁴ These tunnelling rate calculations

were performed using a 1D semi-classical Brillouin-Kramers-Wentzel (BKW) approach.⁷⁸ Given that such calculations are extremely sensitive to small variations in barrier area, this is a remarkable result: for example, we find that changes in barrier height or width by as little as 3% can influence the tunnelling rate by a factor of 2 or more. This therefore provides a strong indication of the accuracy of the excited state potentials generated for phenol by the CASPT2 method in this instance. Comparing our EOM-CCSD calculations for phenol to the CASPT2 result, we find that our approach underestimates the S_1/S_2 CI barrier height by ~ 0.2 eV. However, our data does produce a very similar O–H bond distance at which this CI is located (~ 1.2 Å), and the shape of both the S_1 and S_2 potentials are qualitatively correct. We therefore take the potential cuts shown in Figure 10 to be sufficiently reliable to facilitate a qualitative discussion of the change in barrier characteristics across the 4 molecules used in this present study. This is the key factor of relevance to the interpretation of our data. It is therefore interesting to note from Figure 10 that the barrier area (with respect to the O–H zero-point energy) is approximately an order of magnitude smaller in catechol than in phenol, resorcinol or hydroquinone.

IV. DISCUSSION

As already outlined in the Introduction, numerous dynamical studies of relevance to this current work have been performed on the phenol system. A recent study by Ashfold and co-workers has also revealed broadly similar dynamical signatures in catechol.⁵⁷ Although some subtle differences are seen in these two systems, the same basic relaxation pathways appear to be in operation. In addition to these previous observations, our supporting calculations suggest the same (and no other) electronic states are energetically accessible in resorcinol and hydroquinone. For all four systems under study in this present work, several key common features are also seen in the experimental data (i.e., two time constants in all cases with the associated DAS overlapping the same spectral region, and similar PADs with similar time-dependent evolution). In the following discussion we therefore assume that the basic relaxation pathways present in all four molecules are the same – although some clear differences also exist, which will be rationalised in due course. On the basis of this notion, we therefore frame our interpretation in terms of the dynamical timescales observed, rather than considering the overall dynamics of each individual molecule in turn. We begin with the long-time dynamics. Although this may seem like a counter-intuitive starting point, we believe that, for clarity and brevity, this is a logical approach given the nature of the available dynamical information already determined in previous work.

A. Long-time (> 10 ps) dynamics

There now appears to be strong evidence that, at excitation wavelengths longer than 248 nm, one decay pathway for the initially prepared S_1 state of phenol is via tunnelling under the barrier formed by the S_1/S_2 CI along the O–H stretch-

ing coordinate. This may be induced by vibrational modes of a_2 symmetry, with odd-quanta excitation of the ν_{16a} ring torsion mode being identified as playing a significant role.³⁴ Excitation of spectator modes (i.e., those orthogonal to the tunnelling coordinate) does not appear to influence the tunnelling lifetime and a second, as yet not fully characterised pathway has also been suggested, mediated by the spectator modes and leading to the observed decay in overall S_1 lifetime with increasing excitation energy.¹⁴ At the 267 nm pump wavelength used in our present study, we are sitting ~ 2850 cm^{-1} below the (experimentally determined) S_1/S_2 CI and are not able to access the S_2 state directly. Given that structured fast H atom distributions have also been observed by Ashfold and co-workers in this energy region (see Table II of Ref. 28), we therefore must reasonably ascribe at least some portion of the long-lived ($\tau_2 = 980$ ps) time-constant in phenol to decay of the S_1 state via a tunnelling mechanism. For this process to occur, vibronically induced mixing of the S_1 and S_2 states is required and strong evidence for this interaction is evident in the highly anisotropic ($\beta_2 \sim 0.9$) PADs we observe, even at very long pump-probe delay times: in the Franck-Condon region, the S_2 state is known to exhibit significant $3s$ Rydberg character.¹⁹ At a first (i.e., atomic-like) level of approximation, single photon ionization of a $3s$ orbital should therefore give rise to photoelectron partial waves of exclusively p character, peaking along the laser polarization axis. This is what we indeed observe, as illustrated in Figures 5 and 6, suggesting that the S_1 state contains significant S_2 electronic character. This also corroborates well with the fact that we observe no significant contribution to the PADs from a β_4 component as the s -orbital character of the S_1 state can possess no initial alignment. It also explains why no decrease in β_2 is observed over time as a possible consequence of rotational dephasing in the initially prepared S_1 state. In contrast, we in fact see an increase in β_2 during the initial (i.e., < 1 ps) dynamical evolution, as evidenced in Figure 9 – an observation we shall return to consider shortly. On the grounds of symmetry, vibronic interactions between S_1 and S_2 are mediated by vibrational modes of a_2 symmetry. Since such modes are not accessible directly in single-photon absorption, this suggests that some element of intramolecular vibrational redistribution (IVR) is required to promote this mixing and hints at the possible origin of the short time dynamics we see in our data (*vide infra*). Our value of $\tau_2 = 980$ ps for the overall S_1 lifetime following 267 nm excitation lies between the values reported by Stavros and co-workers at 275 nm and 258 nm (1900 ps and 900 ps respectively).¹⁴ Although this earlier work only required a single decaying exponential function to fit the observed parent ion transients, these authors have also observed a bi-exponential decay in unpublished data recorded at 267 nm, in agreement with our own findings.⁷⁹ Since the overall S_1 lifetime is shorter than the observed tunnelling lifetime (2.4 ns) reported in the same work, another, significant competing pathway for long-time decay of the S_1 state is also likely to be operative, with a rate that increases to shorter excitation wavelengths. However, given that our current experiments are “blind” to the population of lower lying, highly vibrationally excited electronic states (such as S_0) due to unfavourable Franck-Condon overlap with

the cation, we are unable to comment on this further and it remains an open question.

In the case of catechol, the overall S_1 lifetime is dramatically reduced relative to phenol (12.1 ps vs. 980 ps), although it is still sufficiently long-lived to suggest that at 267 nm we are not in a regime where significant direct excitation to the dissociative S_2 state (with subsequent prompt dissociation along the O–H stretching coordinate) is taking place. Ashfold and co-workers have postulated that the onset for such direct excitation may lie between 270 and 265 nm (i.e., at a lower energy, relative to the S_1 origin, than in the case of phenol) and that a very similar H atom tunnelling mechanism to that present in phenol is operative at longer excitation wavelengths.⁵⁷ Our supporting calculations presented in Figure 10 clearly show a considerable reduction (by an order of magnitude) in the area under the barrier formed by the S_1/S_2 CI along the O–H stretching coordinate. On the basis of this evidence it therefore is reasonable to rationalize the major decrease in the S_1 lifetime in catechol (when compared to phenol) to an increase in the tunnelling rate (of the non-hydrogen bonded H atom) due to the suppression of this barrier. As with phenol, this process appears to be mediated by a vibronic interaction that mixes the electronic character of the two states, as is evidenced by the time-dependent evolution of the anisotropy in the catechol PADs. However, we should point out here that, as in the case of phenol discussed in the Supporting calculations section, our EOM-CCSD calculations must be underestimating the true barrier height in catechol; in this case by ~ 0.15 eV. Nevertheless, the calculations appear to provide a good qualitative explanation of our observed experimental data. Our overall catechol S_1 lifetime of 12.1 ps is also in good agreement with very recent, and as yet unpublished data from the Stavros group: at 267 nm excitation, they observe lifetimes of 11.5 ps and 10.5 ps for the overall S_1 lifetime (obtained from a transient ion-yield measurement) and fast H atom appearance time (characteristic of dissociation on the S_2 surface), respectively.⁷⁹ Of potentially more significance is the fact that this group have also observed the fast H atom appearance time to be largely invariant over the 280.5–250 nm excitation range. This appears to suggest that tunnelling always proceeds exclusively from the zero-point energy of the O–H coordinate. Such an assertion clearly places the S_1/S_2 barrier at considerably higher excitation energy (comparable to phenol), which appears to be inconsistent with the relatively short lifetimes observed. In contrast to the other three systems investigated in this present study, the S_1 state of catechol is known to be non-planar, with the non-hydrogen bonded OH group pointing out of the plane defined by the rest of the molecular framework.⁴² The role of OH torsional excitation within the S_1 state has also been implemented in mediating the catechoxy radical product state distribution following dissociation.⁵⁷ We therefore suggest that interpreting experimental data from catechol with recourse to a simple 1D model directed along the O–H stretching coordinate may be insufficient to fully rationalize the excited state relaxation dynamics, and more expansive theoretical treatments will ultimately be required.

Our calculations predict the height and area under the S_1/S_2 barrier along the O–H stretching coordinate in resor-

cinol and hydroquinone to be very similar to that predicted in phenol. However, the τ_2 lifetimes obtained for resorcinol and hydroquinone are quite different, being >1 ns and 440 ps, respectively. When compared to the corresponding value of 980 ps obtained for phenol, the hydroquinone data seems to be in reasonable qualitative agreement with what might be expected on the basis of our calculations: this is due to the fact that H atom tunnelling may occur along either of the two O–H coordinates present in this system, providing a factor of 2 increase in the overall rate of population loss from the S_1 state. This interpretation is obviously based on the assumption that H atom tunnelling is a major relaxation pathway in this instance but, given that in phenol and catechol such a mechanism is clearly present, this would seem to be extremely likely. This is also supported by characteristic features that are consistent across all of our experimental data, such as the nature of the PAD anisotropy and temporal evolution. In the absence of additional measurements providing information on the dependence of the τ_2 lifetime as a function of excitation wavelength we are, however, unable to comment further on any other possible competing processes (such as the previously discussed $S_1 \rightsquigarrow S_0$ IC pathway driven by spectator modes orthogonal to the O–H coordinate that has been postulated in phenol).¹⁴ This is clearly an issue that can be addressed in future studies. The tunnelling assumption would, at a purely heuristic level, also appear to be reasonable for resorcinol. Given that a factor of 2 increase in tunnelling rate might also be anticipated for this system, the extremely long τ_2 value is difficult to reconcile on the basis of our supporting calculations. However, as discussed earlier, the highly-sensitive exponential dependence of tunnelling rates on barrier characteristics means that even relatively small changes in the energetic positions and/or shape of the S_1 and S_2 potentials may have a profound effect on lifetime. In this instance our calculations may lack sufficient accuracy to fully address these subtleties.

B. Short-time (<1 ps) dynamics

The values of $\tau_1 = 320$ – 990 fs are clearly too long to be attributable to “ballistic” motion of an initially prepared vibrational wavepacket out of the Franck-Condon window, resulting in a decrease in ionization efficiency. As noted previously, we may also rule out excitation to superexcited states on the grounds of our observed photoelectron energy distributions. An alternative possibility is that τ_1 results from some degree of rapid non-adiabatic population transfer to a lower lying electronic state (or states). Time-resolved photoelectron studies of the S_1 state in benzene reported by Fielding and co-workers have observed sub-picosecond dynamical timescales following UV excitation in the “channel 3 region.”^{80,81} This was attributed to two competing relaxation pathways: internal conversion to S_0 and ultrafast intersystem crossing to the T_2 triplet state (with subsequent relaxation *via* T_1). Theoretical calculations suggest that, in both of these instances, the relevant CIs sit along a reaction coordinate where benzene evolves towards prefulvene, which is a non-planar, biradical structure.^{82,83} A similar prediction has also been made for phenol by Domcke and co-workers,²³ although the energetic

barrier to access the prefulvenic decay channel is calculated to be 6370 cm^{-1} , which is more than 2000 cm^{-1} above the S_1/S_2 CI. In the context of this present work, the involvement of prefulvenic type structures rapidly driving population to new electronic states is difficult to reconcile with our experimental observations as the timescale for such a rearrangement of the molecular framework should be highly sensitive to the number and position of substituent groups attached to the benzene ring. This is not supported by the broadly similar τ_1 values seen in all cases and, in particular, the almost identical lifetimes of 720 fs, 990 fs, and 880 fs obtained for phenol, resorcinol and hydroquinone, respectively. Overall, we suggest that (within the “view” of the reaction coordinate(s) afforded by our chosen pump wavelengths) we see no strong evidence supporting the involvement of sub-picosecond IC/ISC pathways to lower lying states in our data, although we note that we can not rule out such a possibility definitively as we are effectively blind to their direct population.

An alternative possibility for the origin of τ_1 in our data is “ultrafast” IVR on the S_1 potential surface leading to a modified Franck-Condon overlap with the cation and an associated decrease (or, in the case of resorcinol, an increase) in ionization signal. Time-resolved IR-UV pump-probe studies by Abel and co-workers, initially populating the CH-stretch overtone or the CH-stretch-CC-stretch combination in the S_0 state of benzene and the difluorobenzenes, have reported a two stage IVR process with an initial redistribution of vibrational energy into “doorway states” taking place on a sub-picosecond timescale.⁸⁴ Subsequent “statistical” or “distributive” IVR was then also observed at longer pump-probe delays. This work also demonstrated that the IVR rate increased in systems possessing lower symmetry, which is a commonly encountered phenomenon due to less restrictive coupling requirements leading to an effective increase in the density of available coupling states. Ultrafast IVR has also been suggested to account for sub-ps dynamical observations on the S_1 potential surface of chlorobenzene.⁸⁵ We therefore suggest that some form of IVR mechanism, mediated by vibronic rather than anharmonic coupling, is the most likely origin of the τ_1 decay seen in our data. For the 4 molecules investigated in this present study, we are sitting $\sim 1100\text{--}3950\text{ cm}^{-1}$ above the S_1 origin, which should be well above the threshold for the onset of such a process in all cases. We note that in hydroquinone this threshold has been experimentally determined to be 1650 cm^{-1} ,⁵³ and that in the S_1 state of anisole (the methoxy-substituted analogue of phenol) it has been reported at 940 cm^{-1} .⁸⁶

An IVR interpretation is also supported by the previously discussed requirement that some form of vibronic interaction must be required to promote the S_1/S_2 mixing that is apparent in the long-lived anisotropy of the PADs we observe – particularly since this mixing is mediated by vibrational modes that are not optically accessible in the initial one-photon excitation.³⁴ The role of IVR also accounts for the shorter τ_1 lifetime (320 fs) seen in catechol relative to the other systems under study as the non-planar S_1 state possesses a lower symmetry than phenol, resorcinol and hydroquinone. Additionally, an IVR mechanism provides a simple explanation for the rising signals seen in resorcinol (and the associ-

ated negative amplitude features present in the τ_1 DAS): in contrast to phenol, catechol and hydroquinone, where vibrational redistribution reduces the Franck-Condon overlap with the cation, in resorcinol it may lead to an increase in some regions of the photoelectron spectrum. Such variations in the extent to which IVR changes the Franck-Condon overlap in photoionization may also explain the mono-exponential decay observed in the phenol ion-yield signal reported by Stavros and co-workers at 258 nm.¹⁴

In phenol and resorcinol, the IVR interpretation also sits well with the observation that τ_1 is well matched to τ_β : coupling into modes that enhance S_1/S_2 mixing (as described by τ_1) leads to an evolution of the S_1 electronic character (as described by τ_β). In catechol ($\tau_1 < \tau_\beta$) and hydroquinone ($\tau_1 > \tau_\beta$) the situation is more complex and we suggest that the differences between τ_1 and τ_β may be attributable to only a subset of the modes populated during the IVR process having an influence on the S_1/S_2 interaction. For the case of all 4 systems under study we therefore attribute the τ_1 lifetime to changes in the *vibrational character* within the S_1 state and the τ_β lifetime to the evolution of the *electronic character* of the S_1 state. We note that similar assertions have previously been put forward in excited state studies of benzene and toluene reported by Suzuki and co-workers.⁸⁷ The fact that different timescales may be observed for these two processes is a powerful illustration of the highly differential nature of the time-resolved imaging approach. Finally, we suggest that we are unable to observe any subsequent second-tier “statistical” or “distributive” IVR processes in our data due to the relatively large number of vibrational states initially populated by the broadband pump pulse used in our experiments. In effect, the initial IVR step is therefore essentially “quasi-statistical” in nature and secondary vibrational energy redistribution does not produce any appreciable further changes in the photoionization cross-section at longer pump-probe delays. Hence our data may be accurately modelled using just two exponential time constants.

V. CONCLUSIONS

Time-resolved photoelectron imaging has been used to investigate S_1 ($\pi\pi^*$) relaxation dynamics following 267 nm excitation in phenol, catechol, resorcinol and hydroquinone, all of which are commonly occurring biological motifs. In all cases we attribute rapid (<1 ps) dynamics to IVR on the S_1 potential surface. This process enhances an interaction between the S_1 state and the nearby S_2 state, which is of 3s Rydberg character in the vertical Franck-Condon region and evolves towards $\pi\sigma^*$ character at extended O–H bond distances. The mixing of this 3s Rydberg character into the S_1 state is readily apparent in the temporal evolution of the highly anisotropic ($\beta_2 > 0$) photoelectron angular distributions we observe. More generally, we suggest that the observation of such anisotropy may provide a strong, direct signature of $\pi\sigma^*$ state participation in the dynamics of many systems containing OH, NH and SH groups, as has been recently illustrated in aniline by Fielding and co-workers.⁸⁸ Such observations will be particularly useful in systems where $\pi\sigma^*$ participation can not always be

unambiguously determined using other (less differential) techniques, a good example of this being our own recent work on indole and 5-hydroxyindole carried out using a magnetic bottle photoelectron spectrometer.⁵⁸ We note, however, that this assertion comes with the caveat that such dynamical signatures may be easily obscured or misinterpreted in situations where multi-photon ionization schemes (potentially proceeding via higher-lying Rydberg states) are employed. The longer time dynamics we observe, characterized by τ_2 , are strikingly different in catechol when compared to the other three molecules under study. On the basis of our supporting calculations, which show the barrier formed by the S_1/S_2 CI along the O–H stretching coordinate to be much lower in catechol than in phenol, resorcinol and hydroquinone, we attribute this to differences in the H atom tunnelling rate under the barrier formed by the S_1/S_2 conical intersection.

Finally, we note that great care must be taken when inferring detailed mechanistic conclusions in complex systems on the basis of studies performed at just a single absorption wavelength. On the other hand, we believe that we have been able to draw on a sufficiently large body of previous work to allow us to present our current interpretation with confidence. Additional studies at an expanded range of pump wavelengths were not possible due to (i) limitations imposed by our current laser set-up, restricting the use of fully tuneable UV output for both the pump and probe beams (ii) our desire, where possible, to perform “clean” experiments where the short-time dynamics are not potentially obscured by probe-pump dynamics evolving to negative time delays, and (iii) our wish to avoid using multiphoton ionization schemes in the probe step, as this can potentially induce transitions to additional, higher-lying electronically excited states – which may obscure the dynamics of interest. This is a particularly significant issue if one wishes to fully exploit the angular information afforded by photoelectron imaging methods. Point (i) will soon be addressed in our laboratory and we therefore hope to perform more expansive, pump-wavelength dependent studies on these systems in due course.

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APPENDIX: IMAGE PROCESSING

In the case of 2D imaging approaches where the entire 3D charged particle distribution is projected onto the imaging

detector, some form of data processing is required in order to extract the velocity distribution associated with a photoionization or photodissociation event. In recent years, numerous strategies for carrying out this operation have been proposed including Fourier-Hankel inversion,^{89–91} iterative forward convolution methods,^{92,93} basis-set expansion (BASEX),^{93–95} backtracking and “onion peeling” techniques,^{96–99} Fourier moment analysis¹⁰⁰ and pattern recognition.¹⁰¹ A direct comparison of several of these (older) methods has been presented by Whitaker and co-workers.¹⁰² In order to perform this step in our data analysis, we make use of the following matrix inversion method, which is similar to that previously employed by Cho and Na within the field of plasma diagnostics.¹⁰³ Let the 3D photoelectron distribution be denoted by $I(x, y, z) \equiv I(\rho, z)$. The projection of this distribution onto the imaging (yz) plane is

$$P(y, z) = \int I(x, y, z) dx. \quad (\text{A1})$$

Using cylindrical coordinates, the cylindrical radius $\rho^2 = x^2 + y^2$ and hence $dx = \rho d\rho / \sqrt{\rho^2 - y^2}$ so that

$$P(y, z) = \int_y^\infty \frac{I(x, y, z) \rho d\rho}{\sqrt{\rho^2 - y^2}}. \quad (\text{A2})$$

To obtain $I(x, y, z)$ from the measured $P(y, z)$, the inverse Abel transform may be used,

$$I(\rho, z) = -\frac{1}{4\pi} \int_r^R \frac{\partial_y P(y, z)}{\sqrt{y^2 - \rho^2}} dy. \quad (\text{A3})$$

However, the derivative in the numerator creates problems with experimental data that contain large amounts of noise and, in such instances, often produces large amplitude spikes (that may be positive or negative) along the centreline of the transformed image. In addition, most inversion techniques are sufficiently slow that, even at low laser repetition rates, they can not be used “on-the-fly” during real time image acquisition with current computing hardware.

The slowness in the explicit evaluation of Eq. (A3) suggests recourse to an alternative method where a great deal of optimization work has been done: matrix inversion. We begin by considering a particular altitude z of a three dimensional charge particle distribution. This may be transformed into a discrete distribution $I(\rho, z) \rightarrow I_{ij}$ by partitioning the xy -plane using lines of constant ρ and constant y , with the index i denoting the maximum radius of the segment and j denoting the maximum y value of the segment, as illustrated in Figure 12. The area of each segment is denoted A_{ij} . The area of the segments touching the x -axis (where $i = j$) is given by

$$\begin{aligned} A_{ii} &= \int_{i-1}^i \int_0^{\sqrt{i^2 - y^2}} dx dy = \int_{i-1}^i \sqrt{i^2 - y^2} dy \\ &= -\frac{1}{2}i\sqrt{-1 + 2i} + \frac{1}{2}\sqrt{-1 + 2i} - \frac{1}{2}i^2 \\ &\quad \times \arcsin\left(\frac{i-1}{i}\right) + \frac{1}{4}i^2\pi \end{aligned} \quad (\text{A4})$$

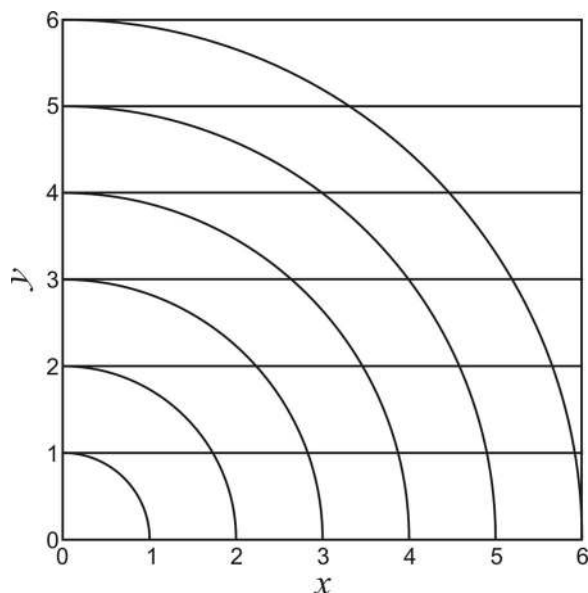


FIG. 12. Partitioning of the plane for Abel inversion. Lines of constant radius ρ and y segment the plane with the area of each segment (the discrete Jacobian) being A_{ij} .

and the area of all other segments is

$$\begin{aligned}
 A_{ij} &= \int_{i-1}^i \int_{\sqrt{(j-1)-y^2}}^{\sqrt{j-y^2}} dx dy \\
 &= \int_{i-1}^i \left(\sqrt{j^2 - y^2} - \sqrt{(j-1)^2 - y^2} \right) dy \\
 &= \left(-\frac{1}{2}j^2 + j - \frac{1}{2} \right) \arcsin \left(\frac{i}{j-1} \right) \\
 &\quad + \left(\frac{1}{2}j^2 - j + \frac{1}{2} \right) \arcsin \left(\frac{i-1}{j-1} \right) \\
 &\quad + \frac{1}{2}i \sqrt{j^2 - 2j + 2i - i^2} - \frac{1}{2}i \sqrt{j^2 + 2i - 1 - i^2} \\
 &\quad - \frac{1}{2} \sqrt{j^2 - 2j + 2i - i^2} \\
 &\quad + \frac{1}{2} \sqrt{j^2 + 2i - 1 - i^2} + \frac{1}{2}i \sqrt{j^2 - i^2} - \frac{1}{2}j^2 \\
 &\quad \times \arcsin \left(\frac{i-1}{j} \right) \\
 &\quad + \frac{1}{2}j^2 \arcsin \left(\frac{i}{j} \right) - \frac{1}{2}i \sqrt{j^2 - 2j + 1 - i^2}. \quad (\text{A5})
 \end{aligned}$$

The projection of the 3D distribution onto the imaging plane at large x is then simply $\mathbf{P} = 2\mathbf{A}\mathbf{I}$ and hence the inverse Abel transform is given by

$$\mathbf{I} = \frac{1}{2} \mathbf{A}^{-1} \mathbf{P}. \quad (\text{A6})$$

Note that the value of I_i represents the average value within the radial segment and not the value at $\rho = i$. However, it is reasonable to approximate the average value to the central value by taking the correspondence $\rho = i - 0.5$.

The main advantage of Eq. (A6) is that there are numerous rapid matrix inversion techniques available. This makes matrix inversion potentially suitable to many real-time imag-

ing applications, as well as the rapid processing of large data volumes. As a rough guide to performance, we are able to invert 100 images (300×300 pixels) in 1 s using standard matrix inversion routines available in MATLAB (The MathWorks Inc, version 7.4.0, 2007a) on a PC with a 2.67 GHz processor using this approach. By way of comparison, the recent polar onion peeling method developed by Roberts *et al.* quotes a processing time for 0.6 s for a single 256×256 image on a 1.7 GHz PC.⁹⁹ This, in itself, appears to represent a speed improvement over other strategies. In addition, least-squares constraints on the solution may be easily imposed (for example, to demand a positive solution everywhere), and routines to perform this operation are readily available in commercial software or may be implemented using, for example, a rapid reflective Newton method¹⁰⁴ or others.¹⁰⁵ Unfortunately, such constraints add significant additional complexity and increase processing time to a large extent. Given that the main appeal of the matrix method is its speed (along with the fact that, in its basic form, it is extremely quick and simple to implement),

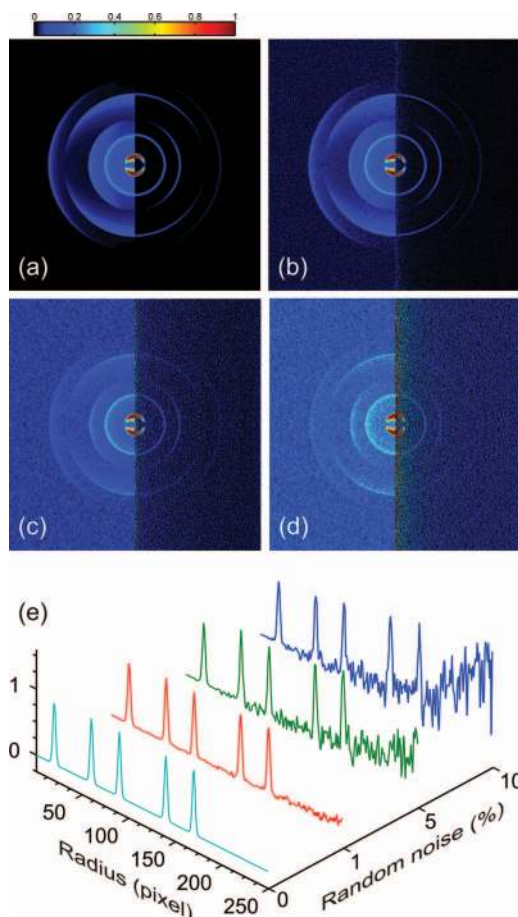


FIG. 13. (a) Synthetic test image comprising 5 rings centred at 20, 60, 90, 140 and 170 pixels. The associated anisotropy is characterised by a single parameter $\beta = 2, 0, -1, 2$ and -1 respectively (where $I(\theta) \propto [1 + \beta P_2(\cos \theta)]$). The cylindrical symmetry axis of the distribution lies in the vertical direction. The left half of the image is the raw data (i.e., a 3D distribution projected onto the 2D imaging plane) and the right half is the result obtained from the matrix inversion method described in the main text. In (b-d) the same image is shown with random noise of up to 1%, 5%, and 10% added to each pixel in the raw data prior to inversion. The reconstructed pixel distributions obtained from images (a-d) are shown in (e).

TABLE II. Results of performing a series of reconstruction tests, as detailed in Ref. 102, on the image shown in Figure 13(a) using the matrix method described in this work. Chapter 3 of Ref. 102 presents the results of the same tests for several other image processing strategies.

Speed (pix.)	Centre deviation (pix.)	Peak width (pix.)	Peak height	Peak area (pix. ²)	Branching ratio (%)	β deviation
20 ($\beta = 2$)	0.25	3.10	0.93	3.596	19.10	0.027
60 ($\beta = 0$)	0.31	3.08	0.98	3.771	20.02	0.029
90 ($\beta = -1$)	0.35	3.06	0.99	3.780	20.17	0.000
140 ($\beta = 2$)	0.48	3.09	0.99	3.832	20.36	0.017
170 ($\beta = -1$)	0.50	3.06	1.00	3.832	20.35	0.000

this approach was not employed in the analysis of the data obtained in this current study. More generally, however, it may be of some interest for processing low signal-to-noise images.

As with many other inversion methods, our approach effectively yields the centre cut through the 3D charged particle distribution and the full velocity distribution may then be obtained by applying a straightforward $R \sin \theta$ weighting to each pixel in the reconstructed image (where R is the pixel radius and $\theta = 0^\circ$ is at the top of the image).¹⁰² In Figure 13(a) we present a synthetic test image (500×500 pixels) consisting of 5 rings, each of equivalent intensity, but exhibiting different degrees of anisotropy. This image is the same as the “cFew” image used by Whitaker and co-workers in their detailed comparison of several different reconstruction methods.¹⁰² Table II summarizes the results we obtain following application of the matrix inversion method when performing the same series of tests that were used in this previous work. In all aspects of the test criteria, the matrix approach performs very well when compared to the other approaches used in the earlier evaluation. In Figures 13(b)–13(d) varying levels of random noise have been added into the image shown in Figure 13(a). Matrix-inverted images are also shown and the corresponding reconstructed pixel distributions are plotted in Figure 13(e). Although no direct comparison with the other schemes used in the tests of Whitaker and co-workers is possible here, the matrix method appears to perform well even with noisy images, and is certainly more than adequate for use with the good quality experimental data obtained in the present study. As with other Abel inversion approaches, the matrix method ultimately suffers from the limitation that it introduces some centre-line noise into the reconstructed images, compromising its effectiveness when compared to some recently developed methods such as the (now widely used) pBASEX approach.⁹⁵ However, matrix inversion is particularly well suited for use in “ultrafast” pump-probe imaging experiments where (i) large data sets consisting of many images are generated and (ii) the spectroscopic resolution is limited by the laser bandwidth rather than any image acquisition/processing considerations.

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