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Solvent induced conformer specific photochemistry of guaiacol†

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Using a combination of ultrafast solution- and gas-phase spectroscopies, together with high-level theory calculations, we demonstrate that we are able to track conformer-specific photodissociation dynamics in solution through solvent choice. We reveal this phenomenon in guaiacol (2-methoxyphenol), a key subunit of the natural biopolymer lignin. In cyclohexane, the first electronically excited \( ^1\text{m}^\pi\text{m}^\pi \) state in guaiacol relaxes with a time-constant of \( \tau = 4.5 \pm 0.2 \) ns, mediated through intersystem crossing to lower lying triplet \( (T_1) \) states and internal conversion and fluorescence back to ground state \( (S_0) \). In contrast, in methanol, a third relaxation channel is also present; the \( S_1 \) state relaxes with a time-constant of \( \tau = 2.9 \pm 0.1 \) ns, which is now additionally mediated through coupling onto a dissociative \( ^1\text{n}_\text{a}^* \) \( (S_1) \) state and subsequent O-H bond fission, evidenced through the appearance of a spectral signature for the guaiacoxyl radical after \( \sim 250 \) ps. With aid of complementary calculations, we attribute this to the now absent intramolecular H-bond between OH and OMe moieties, which now favours intermolecular H-bonding to methanol, lowering the barrier to O-H dissociation and facilitating H-atom loss via tunnelling.

1. Introduction

Conformationally controlled reactions are an intrinsic part of chemistry, be it stereoselective synthesis or protein-folding functionality. Molecular conformers, which may interconvert via rotations about single bonds, have low-energy barriers which are easily overcome following photoexcitation. This presents difficulties if one wishes to track the dynamics of a single, conformer specific photochemical reaction; signal is an ensemble average from the various conformers present. Notable examples, where such specificity was achieved, have been in gas-phase experiments and include conformer driven photodissociation of iodopropane ions,† propanal cations,‡ and morpholine§ and 3-pyrroline.©

Whilst such gas-phase experiments have provided exquisite insight into conformation-specific photochemistry and offer tremendous scope through sequentially increasing molecular complexity to mimic more biologically relevant systems,⁶,⁷ they neglect interactions with surrounding solvent and solute molecules, which are critical to the functionality of many biological systems.⁹,¹⁰ Comparative gas- and solution-phase time-resolved studies are in their infancy,⁸,⁹ but present the tantalising prospect of being able to extend knowledge garnered from key biological chromophores in the gas-phase and integrating this into a more biologically relevant environment. A poignant example, involves the amino acid chromophore phenol. Highly differential gas-phase spectroscopy measurements on phenol¹⁰-¹⁷ coupled with solution-phase UV-pump–UV/visible-probe transient (electronic) absorption spectroscopy (TEAS),²⁰,²¹ have served to emphasise the transferability of knowledge from the gas- to the solution-phase, particularly with regard to its photo-induced O–H bond fission dynamics, which at \( \lambda > 248 \) nm proceeds via an H-atom tunnelling mechanism.¹⁷,²⁰,²²

In this work, we seek to apply this knowledge base to address the role of conformationally driven photodissociation in solution. Conformer specific photochemistry in solution is very well documented in the literature, as exemplified beautifully through excited state intra- and intermolecular proton transfer studies;²³-²⁶ however, examples concerning conformationally driven photodissociation are sparse and here we demonstrate such findings for guaiacol (2-methoxyphenol). Guaiacol is a UV chromophore of lignin, the superabundant natural polymer important to the structural rigidity of vegetal tissues. The
properties of lignin (and its subunits) have been studied extensively, due, in part, to its biological importance and also its industrial potential, such as for use in biofuel production. The addition of a methoxy group at phenol’s ortho position fosters multiple conformers of guaiacol. The structures of the two lowest energy conformers in the gas-phase, termed A and B, are shown in Fig. 1. In the gas-phase, conformer A is the lowest in energy, owing to the intramolecular hydrogen bond between the phenolic hydrogen and methoxy oxygen. Ab initio (gas-phase) calculations have found the interconversion barrier between A and B, to range between 2291 and 2532 cm$^{-1}$. These calculations also determined the energy difference between the two conformers to fall between 1569 and 1670 cm$^{-1}$. Given these energies, one may expect the population of A to be >99% at room temperature in the gas-phase. In a weakly perturbing environment, such as that of a non-polar solvent (e.g. cyclohexane), we would anticipate similar Boltzmann statistics, with conformer A dominating. However, in a highly perturbing environment such as that of a hydrogen bonding solvent (e.g. methanol or H$_2$O), we would anticipate significant population of conformer B as intermolecular hydrogen bonding stabilises conformer B, thus lowering its energy.

Here we present our findings of guaiacol’s conformation specific photochemistry in solution using TEAS following initial excitation to the S$_1$ (ππ*) state with 267 nm radiation. A key finding in our results is that we are able to demonstrate conformational control in the ensuing photodissociation dynamics through choice of solvent, enabling us to effectively switch on O–H bond fission in guaiacol in a polar, H-bonding solvent and switch this process off in a non-polar solvent. In order to explore this conformational control further, we compare our results with highly complementary gas-phase time-resolved photoelectron imaging measurements (TRPEI) and high level complete active space with its second order perturbation theory (CASPT2) calculations, which show that our results in a non-polar solution map on to those observed in vacuo, as one may anticipate from a weakly perturbing environment.

2. Results and discussion

2.1. Transient electronic absorption spectroscopy

TEAS, employing 267 nm (4.64 eV) pump pulses with fluences in the region of 2 ≤ F ≤ 6 mJ cm$^{-2}$ and broadband white-light (340 to 690 nm) probe pulses, was used to record the transient absorption spectra (TAS) of guaiacol in 25 mM solutions of either cyclohexane or methanol flowing through a wire-guided gravity jet, at a range of pump-probe time delays. The chosen concentration ensures a sample absorbance of around 0.5 with a ~125 µm path length. The results of these studies are shown in Fig. 2 and Fig. 3. The time-window of our experiments is set at 2 ns, although we have recorded TAS at longer pump-probe time delays (up to 10 ns) merely serving to confirm any qualitative evolution of key spectral features in our TAS after 2 ns.

TAS of guaiacol/cyclohexane at a series of pump-probe time-delays are shown in Fig. 2(a) and (b), for early (<25 ps) and long (25 ps – 8 ns) delays, respectively. The profile of the TAS is broadband, with two distinctive broad peaks (~340 and ~620 nm) and resembles that seen in analogous studies of phenol in cyclohexane. Based on this, we similarly assign this broad transient absorption signal to excited state absorption (ESA) from the S$_1$ state to higher lying singlet states (S$_n$) – a conclusion made in other similar studies. Cursory inspection shows that as the pump-probe delay increases from 0.5 ps to 2 ns, the TAS decay almost uniformly across the entire spectral window of the probe. We have also included representative TAS for solvent-alone scans at 25 ps and 2 ns, shown in Fig. 2(a), which has a flat absorption profile across 340 – 690 nm and also decays uniformly with increasing pump-probe delay. At the longest time-delay of 8 ns, transient absorption signal in the red end of our probe window (λ > 500 nm) recovers to a base line level of ΔOD = 0, in accordance with complete decay of the S$_1$ ESA as the S$_i$ state is depopulated. However, at λ < 500 nm a broad transient absorption signal, which gradually rises towards the blue end of the spectrum, is seen to persist. Given that the profile is significantly different to the S$_1$ ESA, this must be due to a different absorbing species or state.

It is known that intersystem crossing (ISC) in photoexcited phenol(s) is non-zero in a range of solvents. The ISC quantum
yield ($\Phi_T$) in phenol has been shown to be dependent on solvent polarity, with $\Phi_T$ values for phenol in cyclohexane, acetonitrile and ethanol of 0.27, 0.50 and 0.67, respectively. Differential TAS on phenol, with and without triplet quenching, has also shown the ESA profile of the populated triplet state ($T_3$) to be weakly absorbing, broad and structureless in the range 350 – 475 nm. However, a number of substituted phenols and related species (viz. $p$-cresol and anisole) have remarkably different $T_n$ ESA in this spectral region and display a more sloping character, each rising below ~500 nm with a maximum at ~375 nm, akin to what we observe in Fig. 2(b) at 8 ns. With some confidence therefore, we assign this feature to $T_1$ at ~375 nm, akin to what we observe in the ESA profile of the populated triplet state ($T_n$). The $S_1$ ESA profile decays over time, and once again, at the longest time delay of 10 ns, a similar $T_n$ ESA signature is observed, although this appears to be larger and spans a greater region of our probe window in methanol. Given the increasing $\Phi_T$ trend observed in phenol as a function of increasing solvent polarity (vide supra), this may explain the relative difference in size of the $T_n$ ESA signal seen in guaiacol/cyclohexane versus guaiacol/methanol solutions at >8 ns.

We have repeated these TEAS measurements with methanol as the solvent, and the obtained TAS are shown in Fig. 3(a) and (b). The profiles of the TAS are broadband and generally possess the same characteristics as the $S_1$ ESA seen in cyclohexane. However, the TAS recorded for guaiacol in methanol between 0.5 – 25 ps (Fig. 3(a)) differ from those recorded in cyclohexane (Fig. 2(a)) in that there is a noticeable increase in the relative size of the absorption profile in the red end of the probe spectrum versus that of the blue. This is reconciled by looking at the solvent-only scan for methanol at 25 ps in Fig. 3(a) (dark grey line), which has a clear bias toward the red end of the probe spectrum, and is itself time-dependent, as demonstrated by the solvent-only scan for methanol at 2 ns in the same figure (light grey line).

Spectra at later time delays (25 ps to 2 ns) are shown in Fig. 3(b) and also show a similar trend to those obtained for guaiacol in cyclohexane. The $S_1$ ESA profile decays over time, and once again, at the longest time delay of 10 ns, a similar $T_n$ ESA signature is observed, although this appears to be larger and spans a greater region of our probe window in methanol. Given the increasing $\Phi_T$ trend observed in phenol as a function of increasing solvent polarity (vide supra), this may explain the relative difference in size of the $T_n$ ESA signal seen in guaiacol/cyclohexane versus guaiacol/methanol solutions at >8 ns.

Whilst the guaiacol/methanol and guaiacol/cyclohexane TAS are largely similar, notable differences are present. In particular, one can clearly discern a new spectral feature emerging from ~250 ps onwards, with two peaks centred at 368 and 383 nm, in the guaiacol/methanol TAS, which are absent within the signal-to-noise of the guaiacol/cyclohexane measurements, as highlighted with grey dashed lines in Fig. 3(b). Nanosecond TEAS studies of guaiacol/tert-butoxy radicals mixtures in acetonitrile reveal that the guaiacyloxyl radical ($\text{[C}_6\text{H}_4\text{O}(\text{OCH}_3)(\text{O})]$) has a vibrationally structured absorption feature around 380 nm (with peaks at ~365 and ~381 nm) and a broad absorption at around 650 nm. These are due, respectively, to the $C \leftrightarrow X$ and $B \leftrightarrow X$ electronic transitions in $\text{C}_6\text{H}_4(\text{OCH}_3)(\text{O})$. Whilst the broad absorption band at 650 nm appears to be absent in our TAS, the vibrationally structured features observed at 368 and 383 nm in Fig. 3(b) give us confidence that these are due to the formation of guaiacyloxyl radicals. Potential reasons for the absence of a clear guaiacyloxyl radical absorption signature at ~650 nm may be due to the fact that the $T_2$ ESA and remaining solvent response are significantly masking this feature. This is supported by the TAS collected at 2 ns in a 35 mM guaiacol/chloroform solution (see ESI online) which clearly returns the guaiacyloxyl radical absorption spectrum, including the weaker broad absorption feature at 650 nm due to the $B \leftrightarrow X$ transition. The excited state quenching properties of chloroform are well established and serve to highlight that a combination of solvent signal and $T_2$ ESA is indeed most likely masking the appearance of the weaker broad absorption feature at ~650 nm.

Our TAS of guaiacol in cyclohexane and methanol also allows us to extract an $S_1$ lifetime. Given that the guaiacyloxyl radical absorbs at ~380 nm and ~650 nm, and the $T_2$ ESA signal is present at ~500 nm, integrating a 5 nm wide slice of the TAS centred at 540 nm (where $S_1$ ESA dominates) across pump-probe time-delays from 25 ps to 2 ns enables us to probe the $S_1$ state lifetime with minimal spectral overlap of any possible radical features or $T_n$ ESA; this is shown in Fig. 4. The transients in Fig. 4 are each fit with a multi-exponential function (See ESI for in-depth analysis) to yield time-constants that characterise the lifetime of the $S_1$ state. The results of these fits return $S_1$ lifetimes of 4.5 ± 0.2 ns and 2.9 ± 0.1 ns for guaiacol in cyclohexane and methanol, respectively. The early dynamics (~25 ps) are a convolution of dynamics of the solvent alone in addition to both intramolecular vibrational relaxation (IVR) in
guaiacol and intermolecular energy transfer (IET) between guaiacol and the solvent bath, collectively termed vibrational energy transfer (VET).21,41,42 The kinetic fits also yield timescales for VET of 2.1 ± 0.4 ps and 540 ± 250 fs for guaiacol in cyclohexane and methanol, respectively. In each case this manifests as a small increase in S1 ESA as the Franck-Condon overlap for Sn ← S1 absorption evolves through VET on Sn (presumably giving better overlap between S1 and the Sn states). The faster VET time constant of guaiacol/methanol, relative to guaiacol/cyclohexane, can be rationalised on the basis that the former is an intermolecularly hydrogen bonded system and IET will be significantly increased.38 Whilst these dynamical processes are interesting in themselves, they do not contribute to the main thrust of this work and hence are not discussed further.

2.2. Time-resolved photoelectron imaging

To gain further insight into the mode(s) of decay of the initially excited S1 state in guaiacol, we have also carried out highly complementary TRPEI measurements following excitation at 267 nm and probing at 305 nm. Fig. 5 depicts: (a) the time-dependent photoelectron spectrum, (b) the results of a global fitting analysis to this spectrum using two exponential basis functions and (c) the associated residuals, in which the fit is subtracted from the raw data. The energy axis is plotted in electron binding energy (EBE), given the known adiabatic ionisation potential of guaiacol (IPad = 7.93 eV43). As is evident from Fig. 5(a) and (b), there is very little decay in photoelectron signal intensity across all EBEs within the sampled pump-probe delays (−500 fs to +100 ps), suggestive of very long-lived dynamics in the initially excited S1 state.

Further information of the excited state dynamics from the TRPEI data can be gleaned through the decay-associated spectrum (DAS) shown in Fig. 6(a). The DAS spectrum yields two time components, 3.2 ps and 1.3 ns. The short time component of 3.2 ps, which is positive at low EBE and negative at high EBE (indicative of a flow of vibrational population at early times), is assigned to rapid IVR within S1, mediated by vibrational ‘doorway states’, in accordance with work on several related systems.21,19 We note that this IVR time constant is of the same order as the 2.1 ps VET time constant obtained from the kinetic analysis of guaiacol/cyclohexane TAS, although the latter is faster given that IET is also active in solution. In this instance, the IVR process results in a slight increase in ionisation signal at early delay times beyond zero – see Fig. 5(a) and (b) – due to improved Franck-Condon overlap between S1 and the final guaiacol+ cation state. A similar effect has previously been seen in resorcinol (1,3-dihydroxybenzene).19 The long-time component of 1.3 ns represents a lower limit for the S1 state lifetime of isolated guaiacol (given the limited temporal window of 100 ps for the TRPEI measurements), and broadly agrees with the nanosecond lifetimes extracted for guaiacol in solution from the TEAS measurements and the previously reported gas-phase S1 lifetime of ~7 ns.44 However, the decay mechanisms contributing to this lifetime are more difficult to extract from the DAS alone. TEAS measurements in the weakly interacting cyclohexane solvent might suggest that, in part, S1 → Tn ISC crossing may

![Fig. 4 Kinetic traces for guaiacol/cyclohexane and guaiacol/methanol solutions from 0 to 2 ns, each fitted with a mono exponential decay.](image)

![Fig. 5 (a) Time-dependent photoelectron spectrum (b) its fit and (c) the associated residuals. Time axes are linear between ±500 fs and then logarithmic to +100 ps.](image)

![Fig. 6 (a) Decay-associated spectrum of the TRPEI data (vertical dashed line denotes the ionisation potential), (b) anisotropy parameter β as a function of pump-probe delay, where error bars represent one standard deviation, and (b) inset right half: background-subtracted photoelectron image at a pump-probe time delay of 100 ps and left half: same image after Abel inversion performed using methods outlined in reference 20. Time axis is linear to 500 fs and then logarithmic to +100 ps.](image)
also contribute in the gas phase. In principle, ionisation of any populated T states should be observable using TRPEI, although our measurements here do not extend to sufficient time-delays to indicate whether significant population becomes trapped in T at longer timeframes (viz. ~8 ns in TEAS).

Additional insight into the modes of decay from S1 can also be gained by plotting the photoelectron anisotropy parameter, β2, as a function of pump-probe delay, as shown by Fig. 6(b). In earlier TRPEI studies on phenol (and related derivatives), clear temporal evolution of β2 within the first 100 ps was observed, and was taken as a key reporter of vibronic coupling between the initially excited S1 state and a nearby S2 (1πσ*) state, leading to S1 → S2 internal conversion (IC).19 Here though, the invariance in β2 across all pump-probe delays (and all EBEs), suggests that following initial population of S1, there is no similar mixing of the S1 and S2 states within 100 ps, implying that (i) S1 → S2 IC is unlikely to be an active decay pathway (as concluded in similar studies45) and (ii) other pathways such as fluorescence, IC back to S0, and ISC to T1 are the favoured deactivation mechanisms of the S1 state in guaiacol. We return to discuss this in subsequent paragraphs.

2.3. Conformer specific photodissociation dynamics

We now compare our findings from gas- and solution-phase measurements and begin with a comparison of the TRPEI data and the TEAS measurements in cyclohexane, where conformer A is expected to dominate any observed dynamics in both regimes (vide supra). Both sets of data clearly show that following excitation to the S1 state, population flow out of S1 occurs on a timescale >1.3 ns. The concordance of our gas- and solution-phase measurements is not surprising given that the non-polar, weakly perturbing environment of cyclohexane serves as an adequate (zeroth-order) model for the gas-phase environment.20,21,46 Most notably though, the results of the guaiacol/cyclohexane TAS do not show any clear signature for the formation of guaiacoxyl radicals. This latter observation is particularly critical; previous gas-phase studies on the related species phenol and catechol (1,2-dihydroxybenzene) at 267 nm have shown that the S1 (1ππ*) state decays through coupling onto the S2 (1πσ*) state, which is dissociative along an O–H bond, leading to the production of H-atoms in coincidence with a radical co-fragment.17-19,44,47 This process occurs through a tunnelling mechanism under a conical intersection (CI)48,49 formed between the S1 and S2 states. The absence of any guaiacoxyl radicals in our initial TAS in cyclohexane therefore suggests that, on the timescale of our measurements (extended to 8 ns), no photo-induced O–H bond fission via the S2 state occurs in conformer A. This conclusion is also broadly supported by our TRPEI measurements. One would anticipate an increase in β2 over time (as observed in phenol and catechol19) if non-adiabatic coupling between S1 and S2 were occurring in conformer A of guaiacol, given the 3s Rydberg character of the S2 state in the Franck-Condon region (see Ref. 18 for a more expanded discussion); this is clearly absent in Fig. 6(b), in-line with previous studies on aniline where tunnelling mediated S1 → S2 IC is shut off.45

Whilst conformer A is almost exclusive in the gas-phase, and the weakly interacting ‘gas-phase like’ cyclohexane solution, methanol is a polar, hydrogen-bonding species that is expected to play a significant role in dictating the relative energies of the excited states and solute-solvent hydrogen bonding. Previous semi-empirical calculations of guaiacol in a series of solvents suggest that the conformer distribution moves from A to B with increasing dielectric constant.50 From a theoretical standpoint, when one considers that conformer B may form an H-bond that approaches optimal angle and experiences a larger dipole moment, as well as, the possibility of bifurcated H-bonds, B is likely to experience a stronger H-bond to a solvent molecule than that of the intramolecular H-bond in A. Indeed, FTIR studies have shown that the intramolecular bond may be replaced with an intermolecular

![Diagram](image-url)
one in the presence of a proton acceptor. As a result, we may anticipate that conformer B dominates in guaiacol/methanol solution. Considering this, it is perhaps surprising that a comparison of our TAS collated in methanol, with the TAS in cyclohexane and the gas-phase TRPEI results, yields very good agreement for the S1 state lifetime across these three different environments. In methanol however, there is clear evidence for the formation of guaiacoxyl radical photoproducts (appearing as peaks at 368 and 383 nm), suggesting that an additional process is active in conformer B, which is absent in conformer A — namely photo-induced O=H bond fission into C6H4(OCCH3)(O) + H photoproducts.

In an attempt to better understand these experimental observations of solvent-induced conformer specific photochemistry in guaiacol, we turn to the results of complementary theoretical calculations. These calculations are presented in Fig. 7(a) and show potential energy cuts (PECs) for the electronic ground state (S0), S1 (1π*) and S2 (1σ/) electronic states of (gas-phase) guaiacol, with respect to elongation along the O=H bond (R O=H) in both conformers A (red) and B (blue), at the CASPT2(12,11)/aug-cc-pVTZ level of theory. While these phase calculations inherently lack any account of solvation effects, recent solution-phase work on phenol and thiophenols in cyclohexane and ethanol has demonstrated that such PECs can nonetheless be instructive for aiding the interpretation of TEAS measurements, particularly when benchmarked against complementary gas-phase studies (such as TRPEI here). These calculations return an energy difference of ΔEconf = 1860 cm⁻¹ between conformers A and B in S0, in good accord with previous literature. More generally, the profiles of both sets of PECs are qualitatively similar to those observed in many other phenols along their R O=H coordinates, which are well documented in the literature. Key features include the presence of a CI between the S1 and S2 states (S1/S2 CI) and, at a more elongated bond length, a CI between S2 and S0 (S2/S0 CI). There are however, quantitative differences between the PECs for A and B; most notably, the S1/S2 CI lies ~1 eV above the S0 origin in A, whereas this energy difference is reduced to ~0.7 eV in B. To highlight this more clearly, Fig. 7(b) shows the PECs for the S1 and S2 states rescaled on a ‘relative energy’ axis, such that the S1 origin has been set to 0 eV in both conformers. The larger barrier area in A, relative to B, is a direct consequence of the intramolecular H-bond, which is only present in A.

After excitation to S1 below the S1/S2 CI (viz. 267 nm) in many (but not all) substituted phenols, H-atm tunnelling through the barrier below the S1/S2 CI can occur and lead to O=H bond fission on the S1 surface. As is schematically illustrated by the blue curly arrow in Fig. 7(b). As with these other related systems, the location of the S1/S2 CI will dictate the relative barrier area which must be tunneled through, and control the likelihood of any subsequent O=H bond fission. From Fig. 7(b) it is clear that the predicted barrier area (along R O=H only) in conformer A (red + blue shading) is ~2 times greater than the predicted barrier for conformer B (blue shading only), which will severely reduce the tunnelling probability for coupling between S1 → S2 in A relative to B. Indeed, 1-D tunnelling calculations using a semiclassical Wentzel-Kramers-Brillouin (WKB) model in conjunction with these PECs, return tunnelling probabilities of 2.7×10⁻² and 2.7×10⁻⁵ from the zero-point vibrational level of the OH stretch (ν=0) in S1, which subsequently transform into dramatically different tunnelling lifetimes of 3.5 ms and 3.4 ns for A and B, respectively.

With the findings from these calculations in mind, we can now return to understand our experimental observations of conformer specific dissociation dynamics across our different TEAS and TRPEI measurements. After excitation of conformer A at 267 nm in cyclohexane and the gas phase, VET (or solely IVR in the gas-phase) will occur with a rate kVET, leading to population of the ν=0 level in S0, on the order of a few picoseconds. From here, our calculations suggest that population decay from S1 via tunnelling onto S0 is a kinetically unfeasible relaxation pathway in A, due to the large barrier area under the S1/S2 CI. This prediction is in keeping with our experimental findings from both solution phase TEAS and gas phase TRPEI, which together indicate that decay of the S1 state in A is primarily driven by ISC to T1 (κISC) and IC (κIC) and fluorescence (κf) back to the S0 ground state. In conformer B however, which dominates our methanol TAS, our calculations predict a tunnelling barrier which is half that of A. This significantly reduced barrier area allows tunnelling (κt) to become a kinetically competitive process for S1 population decay in B (occurring in competition with κISC, κf and κIC), and serves to explain the observed production of guaiacoxyl radicals through O=H bond fission in our methanol TAS.

The substantial overlap between the guaiacoxyl radical absorption features and those of the S1 ESA signal in our methanol TAS mean that it is currently non-trivial to deconvolute the precise appearance time of the radical photoproduct, although we note that its signature starts to appear after ~250 ps in Fig. 3(b). By way of comparison, we note that in previous TEAS work on phenol/cyclohexane at 267 nm, the appearance of phenoxyl radicals (also proposed to be formed via tunnelling) was evident after ~1 ns. Despite the convoluted nature of our TAS, simple branched kinetics dictate that the appearance timescale of the guaiacoxyl radical should match the observed lifetime of the S1 state (~3 ns). One may therefore tentatively assert that the S1 lifetime will be commensurate with the appearance time of the guaiacoxyl radical, although we stress that further experiments (such as transient infra-red absorption spectroscopy) are needed to add further weight to this conclusion.

We close by acknowledging that our predictive capabilities of an accurate H-atm tunnelling lifetime in guaiacol (and other systems) are somewhat limited, although our value of 3.4 ns derived from the 1-D PECs in Fig. 7 compares very favourably with the experimentally determined S1 lifetime of ~3 ns for B. More detailed insight into the tunnelling lifetime for B would require knowledge of the multidimensional tunnelling barrier beneath the S1/S2 CI based on more complex calculated
potential energy surfaces, which is beyond the scope of this current work. Perhaps more importantly though, we acknowledge that solvation will also affect the relative energies of the electronic states involved in this process. Nonetheless, the combined theoretical and experimental approaches taken in this study, on the model system guaiacol, serve to re-enforce how different geometric conformations, induced by different solvent environments, can have a profound impact on electronic structure, which dictates the ensuing excited state dynamics. It is clear that combining such geometric and electronic structure information, together with a greater understanding of solvation, will be vital in furthering the comprehension of conformer specific photochemistry in a wide range of photoactive biomolecules and their subunits.

3. Conclusions

In summary we have found the photo-initiated dynamics of guaiacol to be highly conformational specific, which is imparted by the hydrogen-bonding nature and polarity of the solvent. In a solution of guaiacol in cyclohexane, we solely observe relaxation of \( S_1 \) excited state population in conformer \( A \), with a time-constant of \( \tau = 4.5 \pm 0.2 \) ns, which is mediated primarily through ISC to lower lying \( T_n \) states and IC and fluorescence directly back to the \( S_0 \) ground state. Given that cyclohexane is a weakly interacting solvent the dynamics map on to those in the gas phase, where conformer \( A \) also dominates, as verified through highly complementary TRPEI studies. As a result of the intramolecular hydrogen bond in conformer \( A \), which dominates in the ground state, H-atom loss via tunnelling and subsequent guaiacoxyl radical generation is not observed, due to a large barrier to dissociation. Upon solvation of guaiacol in methanol, conformer \( B \) now dominates in the ground state, and intramolecular H-bonding is now replaced by an intermolecular H-bond between the methanol solvent and the OH group. Relaxation of the \( S_1 \) excited state in \( B \) occurs with a time constant \( \tau = 2.9 \pm 0.1 \) ns. The presence of two peaks centred at 368 and 383 nm around \(~250\) ps onwards have been assigned to the formation of guaiacoxyl radical and are attributable to H-atom elimination from the \( OH \) group, mediated by a tunneling mechanism. This process is found to be specific to conformer \( B \) by virtue of the smaller tunneling barrier to dissociation in \( B \), relative to \( A \), as inferred through complementary theoretical calculations. As one may expect, the \( S_1 \) lifetime of \( A \) in cyclohexane matches more closely to the previously reported gas-phase lifetime of \(~7\) ns than that of \( B \) in methanol. The faster \( S_1 \) relaxation time of \( B \) is consistent with the postulate that tunnelling here presents an extra relaxation pathway, in addition to the fact that ISC is more efficient in polar solvents. This result serves to illustrate the importance of the solvent on the geometric structure, which converts an intramolecular H-bond to an intermolecular H-bond, essentially resulting in a ‘free’ O-H bond, which can then undergo H-atom elimination, akin to previous studies in related systems such as phenol and catechol.

The role that the solvent plays in determining geometric structure is clearly evident through these model studies. Further work of this nature will surely pave the way to increasing our understanding of how solvent-induced structural changes in photoactivatable biomolecules can manipulate the ensuing excited state dynamics, and ultimately, the species’ biological function.

4. Experimental

4.1. Solution phase methods

Transient absorption data were recorded using our TEAS setup. For the purposes of this experiment, 25 mM solutions of 2-methoxyphenol (98%, Sigma-Aldrich) in either cyclohexane (99.7%, VWR) or methanol (99.9%, Sigma-Aldrich) were delivered using a liquid wire-guided gravity jet based on the design of Tauber et al which provides a fresh sample volume, \(~125\) \( \mu \)m sample thickness, at a sampling rate of 1 kHz. Sample was recirculated using a peristaltic pump (Masterflex) with PTFE tubing throughout. A large (250 ml) sample vat was used to reduce concentration variance due to sample evaporation and degradation.

Femtosecond laser pulses derived from a commercial 1 kHz Ti-sapphire regenerative amplified laser system (Spectra-Physics, Spitfire XP) are split to give two 800 nm beams: (i) 950 mW and (ii) 5 mW. Pump pulses at 267 nm (4.64 eV) are generated from (i) through second and then third harmonic generation using two beta-barium borate (BBO) crystals. The pump beam was focused \(~12\) mm behind the sample, giving a mean beam waist at the sample of \(~500\) \( \mu \)m. White light continuum (340 to 690 nm) probe pulses are generated by focusing an attenuated (ii) into a vertically translated CaF\(_2\) window. Pump-probe delays up to 2 ns are achieved using a motorized optical delay line in the probe beam path. Longer time delays for this experiment (2 to 10 ns) were made using a delay line consisting of movable mounts on pre-positioned magnetic bases spaced 2 ns apart.

4.2. Gas phase methods

The TRPEI setup has been described in detail elsewhere. 2-methoxyphenol (98%, Sigma-Aldrich) was placed in a cartridge mounted within the body of an Even-Lavie pulsed valve and introduced into the spectrometer using helium (3 bar) as a carrier gas. The valve temperature was regulated at 60 °C. After passing into the main interaction chamber the molecular beam was intersected by co-propagating UV pump and probe pulses produced from the fundamental output of a 1 kHz Ti:Sapphire laser system (Spectra-Physics, Spitfire XP). The pump beam (267 nm, 0.1 \( \mu \)J/pulse) was provided by the third harmonic of this output. The probe beam (305 nm, 0.9 \( \mu \)J/pulse) was generated by twice frequency doubling the signal beam output from an optical parametric amplifier (Spectra Physics, OPA-800C). Thin BBO crystals were used as the non-linear medium. Pump-probe temporal delay was controlled using a linear translation stage running under PC control. The two beams were combined on a dichroic mirror and focused into the spectrometer using a 25 cm fused silica lens.
Pump-probe ionisation of the sample took place between the electrodes of an electrostatic lens set-up optimised for velocity-map imaging. A 40 mm MCP/P47 phosphor screen detector was used in conjunction with a CCD camera (640 × 480 pixels) to image the resulting photoelectrons. A pump-probe cross correlation of 160 ± 20 fs was obtained directly from non-resonant (1 + 1) ionisation of pyrrole and energy calibration data was obtained from three-photon, non-resonant ionisation of xenon. Pump-probe delays between −500 fs and +500 fs were sampled in 50 fs increments with a further 20 exponentially increasing steps taken out to +100 ps. At each repeatedly sampled delay position, pump alone and probe alone images were also recorded for background subtraction.

4.3. Theoretical calculations

Using the MolPro 2010.1 computational package the minimum energy geometry of the ground state guaiacol molecule was optimised using complete active space self-consistent field (SA4-CASSCF) coupled with a contracted aug-cc-pVTZ basis set. Extra sets of even tempered s and p diffuse functions were added to the oxygen atoms (ratio=2) in order to describe the Rydberg-valence coupling more effectively. The choice of active space was heavily dependent on the O–Me and O–H ring substituents and after careful testing, an optimal active space of 12 electrons in 11 orbitals was chosen as a compromise between accuracy and computational expense. These orbitals comprised the three π bonding and three π* anti-bonding Hückel type orbitals centred on the phenyl moiety, the πs lone pair centred on the oxygen atoms of the O–Me and O–H groups, the σ and σ* orbitals centred around the O–H moiety and the 3s Rydberg orbital centred on the oxygen atom of the O–H group.

Unrelaxed (rigid body) potential energy scans were then computed along the O–H bond extension coordinate (R\textsubscript{O-H}) using the same basis set as above, but with the more accurate method: complete active space second order perturbation theory (CASPT2). These CASPT2 calculations were based on a SA4-CASSCF reference wavefunction for both the A and B conformations and utilised the same active space as that used for the CASSCF calculations. Since the ground state optimised geometry favours the syn conformation, all other internal degrees of freedom were fixed during the scan along R\textsubscript{O-H}. The PE scans for the B conformer, along R\textsubscript{O-H}, required a 180° rotation of the CCOH dihedral, after which the potential energy was calculated as a function of O–H bond stretch in the normal way with all other internal degrees of freedom fixed at the ground state CASSCF geometry.

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5. Electronic Supplementary Information (ESI) available: guaiacol radical absorption spectrum and fitting procedure. See DOI: 10.1039/b000000x/