Supporting information for:

Exploring the Autoionization and Photo-Induced Proton-Coupled Electron Transfer Pathways of Phenol in Aqueous Solution

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Experimental Apparatus

The experimental apparatus has been detailed previously.[1] Briefly, 267 nm pump pulses were generated by sum-frequency mixing the 800 nm fundamental from a Coherent Legend (30 fs, 32 nm bandwidth, 1 kHz) and its second harmonic, 400 nm, in a type-II BBO crystal, yielding a bandwidth of 2 nm and a pulse duration of 100 fs. 200 nm pump pulses with a pulse duration of 200 fs were generated by sum-fequency mixing the 267 nm and the 800 nm fundamental in a type-I BBO crystal. All experiments employed pump pulse energies in the range 0.4−1.2 μJ with a pump spot size between 100−250 μm (FWHM). TA signals from water solvent were negligible under these experimental conditions for 267 and 200 nm pump pulses. Pump fluence studies established that all TA signals scaled linearly with pump laser intensity over the range of pulse energies used. Broadband white light super-continuum probe pulses were generated by focusing a small portion of the 800 nm fundamental into a rotating CaF_2 disk. The probe pulse was focused into the sample using an off-axis parabolic mirror to a spot size of approximately 50 μm (FWHM). The relative pump−probe pulse polarization (magic angle, 54.7°) was controlled by rotating the electric field vector of the 800 nm fundamental used to generate the super continuum light via a zero-order half waveplate. The polarization purity of the continuum was determined to be >150:1 across the whole probe range (310− 650 nm), and that of the pump pulses >100:1, as measured by the extinction of the light through a calcite polarizer. All TA experiments employed a wire-guided gravity jet to deliver phenol solutions with a linear flow rate of 1 mm ms^{-1}, ensuring that successive laser shots (1 ms time separation) interrogated a fresh sample. [2] The instrument response function at the two pump wavelengths was determined by cross-correlation of the UV pump and white light super-continuum probe to be 110 fs and 200 fs for 267 nm and 200 nm pump wavelengths, respectively. Phenol (99.5%, Avocado Research Chemicals) was dissolved in distilled deionized H_2O (Millipore) and D_2O (Cambridge Isotope Laboratories) without further purification, to make 18 and 90 mM solutions. ^{1}H NMR and FT-IR were used to follow the exchange of the OH functional group to OD when samples were prepared in D_2O instead of H_2O. The spectra revealed negligible signatures of phenol-h_6 and could be entirely assigned to phenol-d_1.

To extract the solvated electron quantum yield arising from 200 nm irradiation of an aqueous solution of phenol, a calibration was performed using the known photodetachment quantum yield for OH⁻.[3,4] An aqueous solution of NaOH with an absorbance at 200 nm equal to the phenol solution was prepared. Sequential transient absorption experiments were then carried out for these two solutions under identical experimental conditions. From the relative ΔOD signal at λ_{probe} = 600 nm and t = 2 ps (a pump-probe time delay when the ejected electron has become entirely solvated), the electron quantum yield arising from photoexcitation of phenol in water was determined.

The quantum yield for phenoxyl radical and solvated electron formation following 267 nm excitation was obtained by calibration against the known photodetachment quantum yield for phenolate (PhO⁻).[5] A solution of phenolate (sodium salt) was prepared to match the absorbance at 267 nm of an aqueous solution of phenol. For the phenoxyl radical, the ΔOD signals at 400 nm, obtained from the back-to-back transient absorption experiments, were used to calculate the phenoxyl radical quantum yield.

Transient absorption measurements: 200 nm H$^+$ scavenger experiments
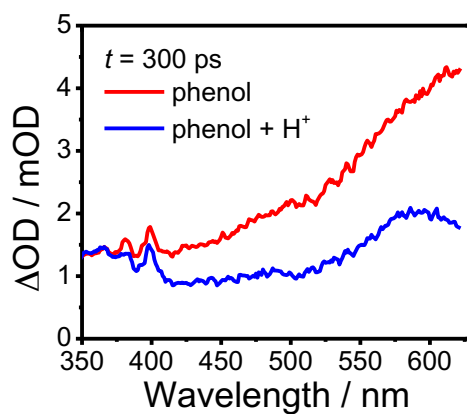
Figure S1 200 nm pump TA spectra for 18 mM phenol-h_6/H$_2$O solution measured at t = 300 ps with (blue line) and without (red line) 0.5 M HCl electron scavengers. The difference in the two spectra identifies the formation of solvated electrons. The small transient at ~580 nm arises from a parallel phenol excimer formation channel, as previously determined.[6]

Free Energy Landscape for Free and Solvated Phenol
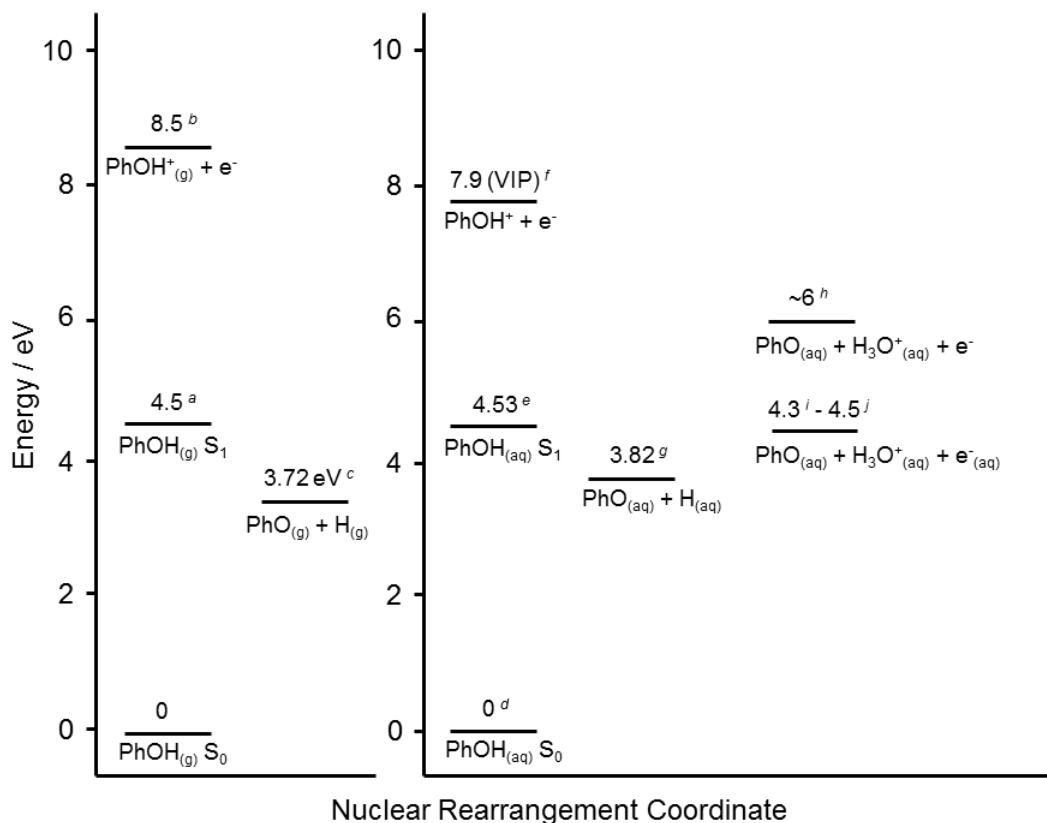
Figure S2 Free energy landscape of phenol and its photoproducts: isolated gas phase molecule (left), aqueous solution (right). The energy (in eV) of each state is labeled on top of the horizontal line.

[a] Gas phase phenol S_1-S_0 origin ($\lambda = 275.113$ nm)[7]

[b] Gas phase phenol vertical ionization potential[8]

[c] Asymptotic value for producing isolated ground state PhO· and H atom radicals[7,9]

[d] The absolute energy of ground state phenol in water is 0.6 eV lower than in the gas phase, due to the solvation enthalpy (ΔH_{solv})[10]

[e] The phenol S_1 origin in water is estimated from the shift in UV absorption spectra between cyclohexane and water solutions

[f] Vertical ionization potential of phenol in aqueous solution[11]

[g] Asymptotic value for producing solvated PhO· and H atom radicals. This value is estimated from the solvation enthalpy of PhO· ($\Delta H_{solv} = -0.4$ eV)[10] and solvation free energy of H atom ($\Delta G_{solv} = -0.1$ eV)[12]

[h] The onset of the photoelectron spectrum for phenol aqueous solution.[11] Note that the free energy release upon proton transfer from phenol cation to surrounding water is small compared to the uncertainty of the position of the onset ($\Delta G = -0.15$ eV)[13], and thus not included in the estimate.

[i] Asymptotic value for producing fully solvated PhO· radical, proton and electron, estimated from the electron attachment energy in water ($\Delta G = -1.54$ eV)[14]

[j] Asymptotic value for producing fully solvated PhO· radical, proton and electron, estimated from the proton transfer from the H atom to water: $H_{(aq)} + H_2O \leftrightarrow H_3O^+_{(aq)} + e^-_{(aq)}$ ($\Delta G = +0.5$ eV)[15]

Transient absorption measurements: 267 nm H$^+$ scavenger experiments
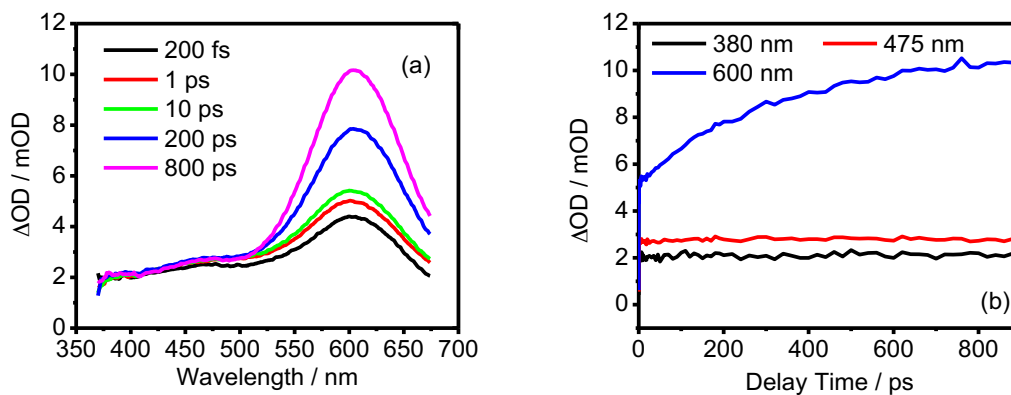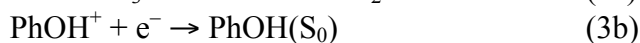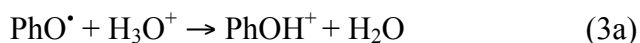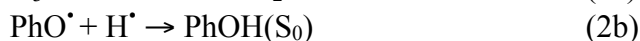

Figure S3 (a) 267 nm pump TA spectra for 90 mM phenol-h_6/H$_2$O solution measured at the displayed pump-probe time delays. (b) Kinetics at selected probe wavelengths obtained from the TA experiment.
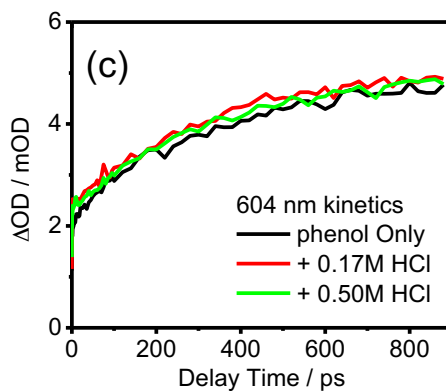
(c) Kinetics of the 604nm feature obtained in 90 mM phenol-h_6/H$_2$O (black), 90 mM phenol/0.17 M HCl (red) and 90 mM phenol/0.50 M HCl (green) solutions.

Possible Geminate Recombination Pathways

The following reactions are all the possible geminate recombination pathways (1-4) that will affect the yield of phenoxyl and solvated electron species in our transient absorption data:

$$PhO^{\bullet} + e^- \rightarrow PhO^-(S_0) \qquad\qquad (1a)$$
$$PhO^-(S_0) + H_2O \rightarrow PhOH(S_0) + OH^- \qquad (1b)$$

$$H_3O^+ + e^- \rightarrow H^{\bullet} + H_2O \qquad\qquad (2a)$$
$$PhO^{\bullet} + H^{\bullet} \rightarrow PhOH(S_0) \qquad\qquad (2b)$$

$$PhO^{\bullet} + H_3O^+ \rightarrow PhOH^+ + H_2O \qquad (3a)$$
$$PhOH^+ + e^- \rightarrow PhOH(S_0) \qquad\qquad (3b)$$

$$PhO^{\bullet} + e^- + H_3O^+ \rightarrow PhOH(S_0) + H_2O \qquad (4)$$

We favor recombination via either reaction 1 or 2, as the product of reaction 3a is known to be unstable (see main paper), precluding reaction 3b. The three-body recombination, reaction 4, is disfavored on entropic grounds.

Process 1a will have the same contact rate as the geminate recombination determined in the photodetachment of phenolate, [5] and will likely be a more important process than reaction 2a; the recombination of two charged products. We rationalize this on energetic grounds; there will be a far larger energy barrier associated with re-organizing the two solvent shells around the separately solvated H_3O^+ and e^- ions, compared to one radical (PhO$^{\bullet}$) and a solvated electron.

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