

Electronic Supplementary Information for: ‘Competing $1\pi\sigma^*$ Mediated Dynamics in Mequinol: O-H versus O-CH₃ Photodissociation Pathways’

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Figures: S1-S5

S11. Resonance Enhanced Multiphoton Ionization Spectroscopy of Mequinol

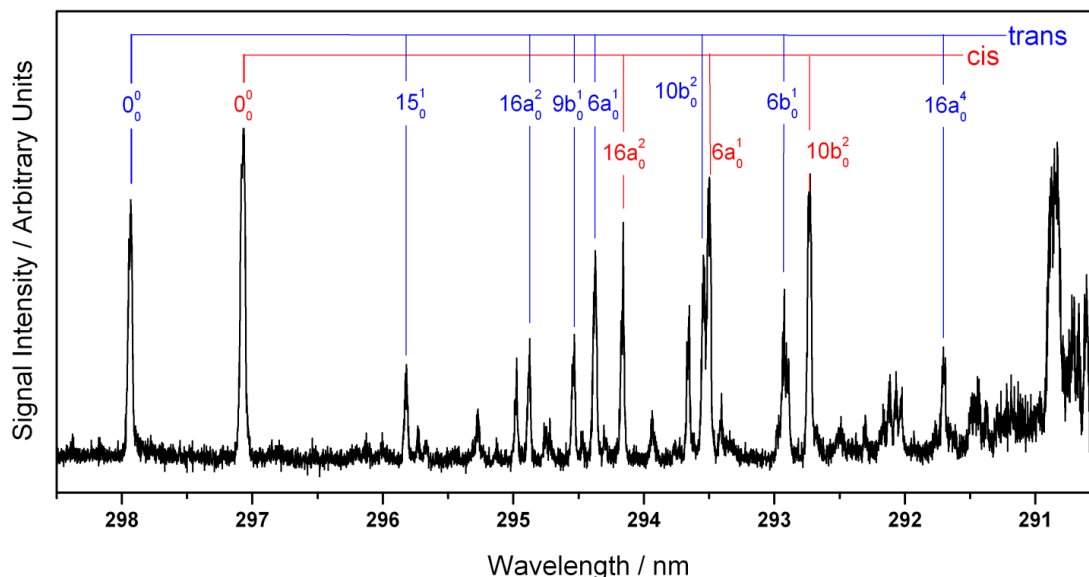


Fig. S1 (1 + 1) REMPI spectrum of jet-cooled mequinol molecules obtained by monitoring the parent ion yield (m/z 124) following ns pulsed laser excitation in the wavelength range 298.5 – 290.5 nm. The evident structure, which matches that reported in a previous laser induced fluorescence study [G. N. Patwari, S. Doraiswamy and S. Wategaonkar, *J. Phys. Chem. A*, 2000, **104**, 8466], arises from population of specific (Franck-Condon active) vibrational levels of the $1^1\pi\pi^*$ state, with the prominent peaks at long wavelength assigned to the $1^1\pi\pi^* \leftarrow S_0$ origins of the *cis* and *trans* conformers, as indicated. The relative intensities of these two peaks are sensibly consistent with that expected on the basis of the relative populations of the two conformers in the heated parent sample.

SI2. Derivation of $D_0(\text{O-H})$ and Comparison of Conformer Dynamics with High Resolution H Rydberg Atom Photofragment Translational Spectroscopy

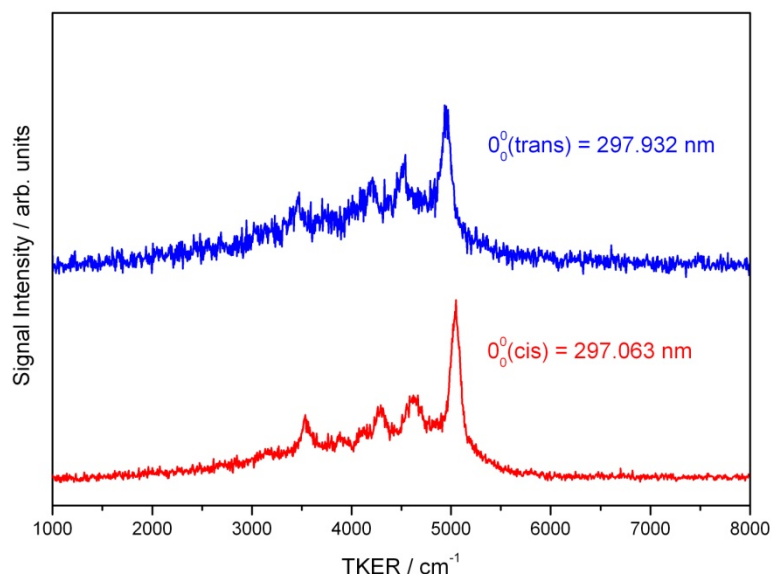


Fig. S2 TKER spectra obtained by monitoring the times-of-flight of H atoms formed following ns pulsed laser excitation of jet-cooled mequinol molecules at 297.063 and 297.932 nm, *i.e.* at the origin of the $1^1\pi\pi^* \leftarrow S_0$ transition of the *cis* and *trans* conformers, respectively. Details of the experiment used to collect such data and of the data analysis methods have been reported previously [Cronin *et al*, main paper ref. 31]. Full analysis, interpretation and discussion of the structure evident in this and many other TKER spectra recorded at other excitation wavelengths (which reflects population of specific vibrational levels within the $\text{CH}_3\text{OC}_6\text{H}_4\text{O}$ co-fragment) yields an O–H bond strength $D_0(\text{O-H}) = 28620 \pm 50 \text{ cm}^{-1}$ [T. N. V. Karsili, A. M. Wenge and M. N. R. Ashfold, unpublished results].

SI3. H^+ Signal Transients at 290 and 298 nm

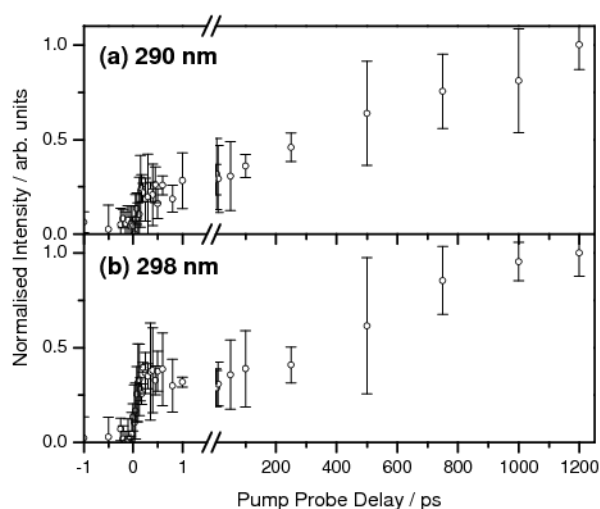


Fig. S3. H^+ signal transients in mequinol, taken at pump wavelengths of (a) 290 and (b) 298 nm, with a probe of 243.1 nm. Transients are obtained by integrating the measured H^+ signal over the TKER range 4000 - 6000 cm^{-1} at a series of pump probe delays. Error bars correspond to two standard deviations (two sigma).

SI4. Calculated H atom Tunneling Rates Beneath the $1^1\pi\pi^*$ / $1^1\pi\sigma^*_{\text{O-H}}$ CI with the Brillouin-Kramers-Wentzel Method

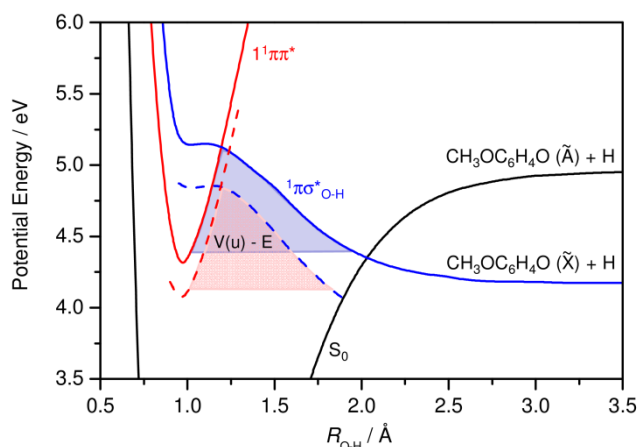


Fig. S4 1-D potential energy cuts, calculated at the CASPT2(12/11)/aug-cc-pVTZ level, along the O-H coordinate ($R_{\text{O-H}}$) in mequinol for the ground state, S_0 (solid black), and first two excited singlet states, $1^1\pi\pi^*$ (solid red) and $1^1\pi\sigma^*_{\text{O-H}}$ (solid blue). Dashed lines are the computed ‘relaxed’ PECs (see text for details). The shaded blue and red areas, labeled $V(u) - E$, represent the barrier area used in 1-D BKW tunneling calculations for the ‘unrelaxed’ and ‘relaxed’ PECs, respectively (see main text for details).

Modeling of H atom tunneling dynamics, accounting for the production of H atoms at 280, 290 and 298 nm, is performed using a semi-classical Brillouin-Kramers-Wentzel (BKW) method with the calculated CASPT2 1-D PECs in Fig. 2(a) of the main paper (‘unrelaxed’ PECs), along the O-H coordinate ($R_{\text{O-H}}$). A similar approach has been applied previously in phenol [Roberts *et al.* main paper ref. 41] and substituted phenols clustered with NH_3 [Pino *et al.* main paper ref. 46]. Previously in phenol however, ‘relaxed’ PECs along the O-H coordinate were used to estimate the H-atom tunneling lifetime. As such, for a more appropriate comparison with our previous studies on phenol, the H tunneling lifetime has also been calculated using ‘relaxed’ PECs in mequinol. These ‘relaxed’ PECs are generated using the methodology described in section 2.2 of the main article, but also include a geometry relaxation of the phenyl ring at each fixed $R_{\text{O-H}}$ distance. Further general details of generating relaxed PECs are reported in ref. 40 of the main paper.

Lifetimes were calculated for H atom tunneling under the $1^1\pi\pi^*$ / $1^1\pi\sigma^*_{\text{O-H}}$ conical intersection (CI) for both the ‘unrelaxed’ and ‘relaxed’ of PECs using the BKW method, which treats the tunneling dynamics within a 1-D approximation along $R_{\text{O-H}}$. The tunneling lifetime (τ), from the zero-point energy (ZPE) of the O-H stretch in the $1^1\pi\pi^*$ state onto the $1^1\pi\sigma^*_{\text{O-H}}$ state can be predicted using:

$$\tau = \left[\nu_{\text{OH}} \exp \left(-2 \int_{u_1}^{u_2} \sqrt{\frac{2m}{\hbar^2} (V(u) - E)} du \right) \right]^{-1} \quad (\text{S1})$$

where u is the O-H bond coordinate, ν_{OH} is the O-H stretch frequency (3740 cm^{-1}), m is the mass of a H atom, $V(u)$ is the potential barrier (taken from the PECs shown in Fig. S4), and E is the kinetic energy of the H atom at the ZPE of the $1^1\pi\pi^*$ state O-H stretch ($\frac{1}{2} \nu_{\text{OH}}$). The calculated ‘unrelaxed’ and ‘relaxed’ PECs (both shown in Fig. S4) generate tunneling lifetimes of ~ 100 and 9.8 ns, respectively. For the ‘unrelaxed’ cut this far exceeds the tunneling lifetime we anticipate from the

experimentally measured H^+ transient in Fig. 3(d) of the main article (a few nanoseconds). However the ‘relaxed’ PECs achieve a value closer to that expected from the experimental data and on the same order of magnitude to that calculated by Roberts *et al.* [main paper ref. 41] in phenol. Shortcomings of the 1-D BKW model for describing tunneling are discussed in the main paper.

SI5. Total Kinetic Energy Release Spectra for H atom Elimination at 254 and 264 nm

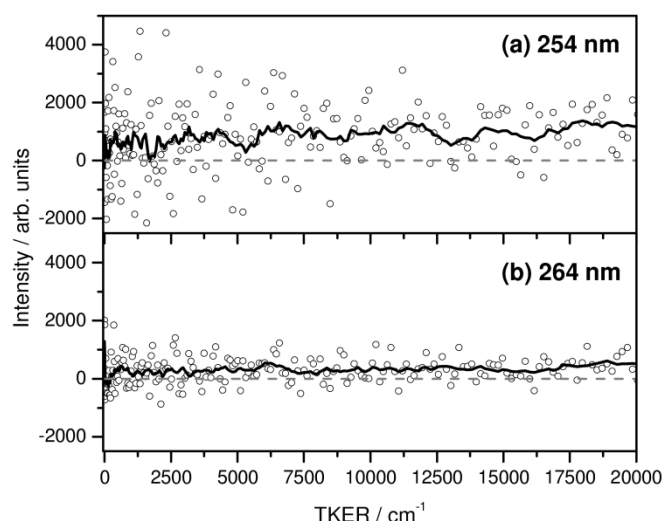


Fig. S5 TKER spectra for H atom elimination in mequinol (circles) at pump wavelengths of (a) 254 and (b) 264 nm, with a 1200 ps delayed 243.1 nm probe. Data is overlaid with a 10 point average (black line).

SI6. Complete Active Space Orbitals and State Transitions

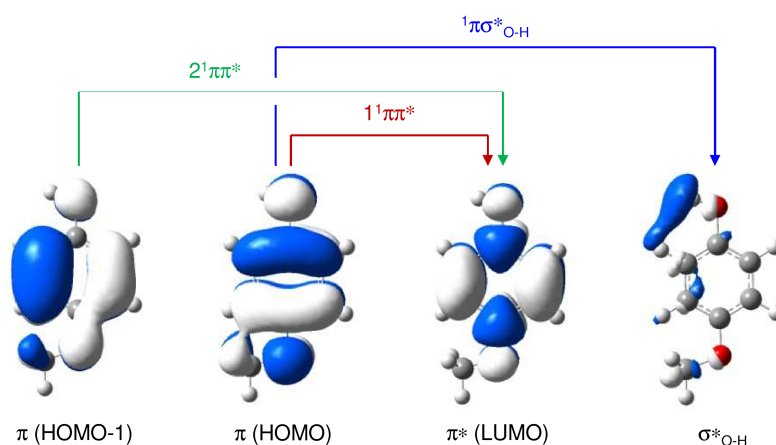


Fig. S6 Optimized complete active space orbitals and calculated dominant transitions associated with the $1^1\pi\pi^*$, $2^1\pi\pi^*$ and $1\pi\sigma^*_{O-H}$ states in mequinol.