Tunnelling under a conical intersection: Application to the product vibrational state distributions in the UV photodissociation of phenols

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When phenol is photoexcited to its $S_1$ ($1^1\pi\pi^*$) state at wavelengths in the range 257.403 $\leq \lambda_{\text{phot}} \leq 275.133$ nm the O–H bond dissociates to yield an H atom and a phenoxy co-product, with the available energy shared between translation and well characterised product vibration. It is accepted that dissociation is enabled by transfer to an $S_2$ ($1^1\pi\sigma^*$) state, for which the potential energy surface (PES) is repulsive in the O–H stretch coordinate, $R_{\text{O-H}}$. This $S_2$ PES is cut by the $S_1$ PES near $R_{\text{O-H}} = 1.2$ Å and by the $S_0$ ground state PES near $R_{\text{O-H}} = 2.1$ Å, to give two conical intersections (CIs). These have each been invoked—both in theoretical studies and in the interpretation of experimental vibrational activity—but with considerable controversy. This paper revisits the dynamic mechanisms that underlie the photodissociation of phenol and substituted phenols in the light of symmetry restrictions arising from torsional tunnelling degeneracy, which has been neglected hitherto. This places tighter symmetry constraints on the dynamics around the two CIs. The non-rigid molecular symmetry group $G_4$ necessitates vibronic interactions by $a_2$ modes to enable coupling at the inner, higher energy ($S_1$/$S_2$) CI, or by $b_1$ modes at the outer, lower energy ($S_2$/$S_0$) CI. The experimental data following excitation through many vibronic levels of the $S_1$ state of phenol and substituted phenols demonstrate the effective role of the $v_{16a}$ ($a_2$) ring torsional mode in enabling O–H bond fission. This requires tunnelling under the $S_1$/$S_2$ CI, with a hindering barrier of $\sim 5000$ cm$^{-1}$ and with the associated geometric phase effect. Quantum dynamic calculations using new ab initio PESs provide quantitative justification for this conclusion. The fates of other excited $S_1$ modes are also rationalised, revealing both spectator modes and intramolecular vibrational redistribution between modes. A common feature in many cases is the observation of an extended, odd-number only, progression in product mode frequencies. A common feature in many cases is the observation of an extended, odd-number only,

I. INTRODUCTION

The role of $\pi\sigma^*$ and $n\sigma^*$ excited states (i.e., states formed by $\sigma^*\rightarrow\pi$ and $\sigma^*\rightarrow n$ electron excitations) is becoming increasingly recognised in promoting non-radiative decay of azoles, phenols, and larger heteroaromatic molecules such as the nucleobases and aromatic amino-acids.$^{1,2}$ Transitions to diabatically bound $1^1\pi\pi^*$ states are understood to comprise the strong UV absorptions associated with such chromophores; however, these molecules also possess low-lying dissociative $1^1\pi\sigma^*$ (and in some cases $1^1\sigma\sigma^*$) excited states. The absorption cross-sections of $\sigma^*\rightarrow\pi$ transitions are typically much weaker, but nonetheless can be populated either by initial excitation to an optically “bright” $1^1\pi\pi^*$ state and subsequent radiationless transfer driven by vibronic coupling at conical intersections (CIs), or in some cases by direct photoexcitation. Once populated, the diabatic $1^1\pi\sigma^*$ state potential energy surface (PES) in these heteroaromatic systems is repulsive with respect to X–H (X = N, O, etc.) bond extension. The lowest $1^1\pi\sigma^*$ state forms a CI with the ground PES at extended X–H bond lengths, $R_{\text{X-H}}$. Figure 1(a) shows cuts through calculated diabatic PESs for these two states of phenol, as well as for the higher $1^1\pi\pi^*$ state ($2^1\pi\pi^*$) and for the first two $1^1\pi\pi^*$ states ($1^1\pi\pi^*$ and $2^1\pi\pi^*$). The latter are bound with respect to $R_{\text{O-H}}$, and the $1^1\pi\pi^*$ PES necessarily experiences a CI with that of the $1^1\pi\sigma^*$ state. The particular focus of this paper centres on the ground, $1^1\pi\pi^*$ and $1^1\pi\sigma^*$ diabatic states which, for compactness, will often be termed $S_0$, $S_1$, and $S_2$, respectively.

The present paper revisits the dynamic mechanisms that give rise to selective vibrational excitation of the radical product evident in the UV photodissociation of phenol and phenolic systems. Domcke, Sobolewski, and co-workers$^{3,6}$ demonstrated theoretically that electron promotion from the highest occupied molecular orbital (HOMO), $\pi$, to the $\sigma^*$ orbital would result in population of the $1^1\pi\sigma^*$ state. Molecules on the $1^1\pi\sigma^*$ state experience a repulsive PES, that

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encourages $R_{O-H}$ extension and eventual O–H bond fission. The $S_2$ state has predominant $3s$ Rydberg character in the vertical Franck-Condon (FC) region, which evolves into purely valence $\sigma^*$ upon extending $R_{O-H}$. Domeke and Sobolewski alternatively proposed that “deactivation” at the $S_2/S_0$ CI could occur instead of bond fission: moving flux in a radiationless transfer to $S_0$.\(^7\)

O–H bond fission in phenol was first experimentally observed (following excitation at a photolysis wavelength, $\lambda_{\text{phot}} = 248$ nm) by detection of translationally excited phenoxyl radicals using multimass ion imaging methods.\(^8\) Our subsequent $H$ (Rydberg) atom photofragment translational spectroscopy (HRA-PTS) studies of phenol clearly identified two different photodissociation mechanisms following excitation at wavelengths longer or shorter than $\lambda_{\text{phot}} = 248$ nm.\(^9\) Exciting the $1^1\pi\pi^*(v = 0)$ level ($\lambda_{\text{phot}} = 275.113$ nm) results in a bimodal $H$ atom time-of-flight spectrum, which after conversion into total kinetic energy release (TKER) space, comprises a set of resolved peaks (centred at TKER $\sim 6000$ cm$^{-1}$) attributable to the formation of $H$ atoms in conjunction with specific and limited vibrational ($v$) levels of the phenoxyl ($\tilde{X}^2B_1$) ground state radical. The second component is structureless and peaks at TKER $\sim 2000$ cm$^{-1}$ (see Fig. 1(b)). This underlying component is attributed to a combination of unimolecular decay on the $S_0$ state after internal conversion (that contributes particularly at low TKERs) and to dissociations following unintended multiphoton absorption and subsequent decay of “superexcited” states.\(^10\) The recoil velocity distributions for both the structured and featureless components formed at this wavelength were found to be isotropic.

Excitation to specific higher $1^1\pi\pi^*$ vibrational levels, at shorter $\lambda_{\text{phot}}$, results in similar TKER spectra. However, the vibrational structure of the phenoxyl products at higher TKER gradually coalesces as $\lambda_{\text{phot}}$ is reduced and was no longer resolvable in spectra recorded at $\lambda_{\text{phot}} \leq 257$ nm. This is illustrated in Fig. 1(c), which shows the TKER spectrum derived from H atom TOF measurements at $\lambda_{\text{phot}} = 240.0$ nm, but careful inspection of this spectrum reveals additional, weak, resolved features at high TKER which become increasingly evident as $\lambda_{\text{phot}}$ is reduced further (Fig. 1(d)). Upon excitation to $\lambda_{\text{phot}} < 216$ nm this structured channel coalesces into a broad unresolved feature centred at TKER $\sim 12000$ cm$^{-1}$. The recoil velocity distribution of the fast $H$ atoms formed at $\lambda_{\text{phot}} < 240$ nm is anisotropic ($\beta \sim -0.5$) implying that O–H bond fission occurs on a timescale that is faster than the parent rotational period, and that the $H$ atom recoils preferentially along an axis that is almost perpendicular to the parent transition dipole moment. This step change in product energy disposal is seen to correlate with whether the excitation wavelength samples energies above or below $\lambda_{\text{phot}} \sim 248$ nm, which we associate with the excitation energy of the $S_1/S_2$ CI.\(^9\)

The focus of the present work is the detailed dissociation mechanism of phenol molecules following excitation to vibrational level of the $S_1$ state and particularly from its $S_1(v = 0)$ level. The $S_1 \leftarrow S_0$ transition shows resolved rovibrionic structure.\(^11,12\) The fluorescence lifetime ($\tau_f$) of the $S_1(v = 0)$ level of phenol-$h_\beta$ is $\sim 2$ ns.\(^13\) Sur and Johnson\(^14\) used pump-probe techniques to estimate the quantum yields and rates for competing internal conversion (IC) and intersystem crossing (ISC) processes from this level. They proposed that IC is the dominant non-radiative decay process and $S_0$ levels that have substantial O–H stretching motion (henceforth denoted as $S_0^\delta$) act as efficient acceptor modes.

HRA-PTS results obtained at $\lambda_{\text{phot}} > 257$ nm (e.g., Fig. 1(b)) were consistent with such a mechanism, and we have previously rationalised dissociation from the $S_1(v = 0)$ level in terms of IC to such $S_0^\delta$ levels and subsequent

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**FIG. 1.** (a) Sections (along $R_{O-H}$) through the calculated (CASPT2/10/10/aug(O)-AVTZ) “unrelaxed” PESs for the $S_0$, $1^1\pi\pi^*(S_1)$, $1^1\pi\sigma^*(S_2)$, $2^1\pi\pi^*(S_3)$, and $2^1\pi\sigma^*(S_2)$ states of phenol. The calculated EOM-CCSD transitional dipole moments for the $S_1 \leftarrow S_0$ (perpendicular to C–O) and $S_1 \leftarrow S_0$ (parallel to C–O) excitations are superimposed on the phenol structure. (b), (c), and (d) show TKER spectra arising from excitation of jet-cooled phenol molecules at $\lambda_{\text{phot}} = 275.113$, 240, and 218 nm, respectively.
O–H bond extension to enable coupling around the lower cone of the S0/S2 CI and dissociation to H + phenoxyl-h3(X)b products.\textsuperscript{9} The S1(v = 0) level of phenol-d1 (C6D2O2D) has a markedly longer fluorescence lifetime (τf \sim 16 ns)\textsuperscript{15} and PTS studies of phenol-d2 revealed no fast D atom products when exciting the S1(v = 0) level. Both observations could be rationalized in terms of much poorer overlap with the S0(high vOD) overtone levels into which flux might internally convert from the S1(v = 0) level.\textsuperscript{9}

Pino et al. have recently used picosecond laser pump-probe methods to determine the lifetimes of the S1(v = 0) levels of bare phenol and several substituted phenols.\textsuperscript{16} The measured lifetimes support an earlier interpretation \textsuperscript{4} for the observed short τf and H/D dissociation yields. In this alternative picture, phenol molecules excited to S1 vibrational levels are considered to dissociate by H atom tunnelling through the barrier under the S1/S2 CI. Such a model is also consistent with the observed H/D isotope effects in phenol-h3 and phenol-d3 (with respect to both τf (Refs. 13 and 15) and the H/D product yield\textsuperscript{9}), and with correlations between the measured S1(v = 0) lifetimes—for a range of substituted phenols and their complexes with NH3—and the calculated vertical energy separations between their respective S1 and S2 PESs.\textsuperscript{16}

Analysis of numerous TKER spectra from phenol-h3 photolysis in the range 275.113 ≥ λphot ≥ 216 nm leads to the conclusion that in no case, does dissociation result in H + phenoxyl(X)b fragments.\textsuperscript{9} An internally consistent O–H bond strength was only obtained by associating the fastest peak in TKER spectra recorded at long λphot (e.g., λphot = 275.113 nm, Fig. 1(b)) with formation of H + phenoxyl fragments carrying one quantum in vibrational mode ν16a\textsuperscript{17} —an out-of-plane (α2 in C2v) ring torsion mode—while, in PTS spectra recorded at λphot < 248 nm (e.g., Fig. 1(d)), the fastest TKER peak had to be attributed to H + phenoxyl radicals carrying one quantum of an alternative ring torsion vibration, ν16b(β1).\textsuperscript{3} Such assignments enabled a consistent value of the O–H bond strength: D0(H–phenoxyl-h3) = 30015 ± 40 cm\textsuperscript{−1}. Analogous vibrational assignments are also applicable to a range of substituted phenols such as p-fluorophenol,\textsuperscript{18} p-methylphenol,\textsuperscript{19,20} and phenol-d3.\textsuperscript{21}

Here we report 2D dynamic simulations utilizing new \textit{ab initio} PESs with a larger basis set than employed previously, which show that the O–H bond fission mechanism based on 11ππ*(S1) \rightarrow 1πσ*(S2) tunnelling enunciated by Pino et al.\textsuperscript{16} provides an interpretation not just for the measured variations in the value of τf for a range of substituted phenols, but can also account for the specific product vibrational energy disposal observed when exciting phenol, and a range of substituted phenols, at photolysis energies below (and above) the S1/S2 CI.

II. \textit{AB INITIO} CALCULATIONS

The ground state geometry of phenol was optimized using complete active space self consistent field (CASSCF) methods. A ten electrons in ten orbitals (10/10) active space, similar to that used by Lan et al.,\textsuperscript{6} was employed. Our active space used the three ring π orbitals, the conjugated oxygen p\textsubscript{x} lone pair, and the O–H σ occupied orbitals, and three π*, the O–H σ* and the oxygen centred 3s Rydberg virtual orbitals. Potential energy cuts (PECs) through R0–H stretch were calculated for the S0, 11ππ*, 21ππ*, 11σσ*, and 21πσ* electronic states using the complete active space with second order perturbation theory (CASPT2) based upon a fully state averaged (SA-CASSCF) reference wavefunction with the ring phenyl geometry frozen at the optimized ground state geometry. In all CASPT2 calculations, a small imaginary level shift (0.5 a.u.) was required to assist convergence and avoid intruder state problems. For all calculations employed within this study, an aug-cc-pVTZ basis set was used with extra even tempered sets of s and p diffuse functions on the oxygen atom (henceforth labelled aug(O)-AVTZ) to better describe any Rydberg-valence mixing. This basis set uses a triple zeta rather than the (inferior) double zeta basis set used in previous studies of phenol,\textsuperscript{3,6,7} and extra diffuse functions on the O atom, which were not included in our previously reported PES.\textsuperscript{21} In addition, “relaxed” scans along R0–H for the 11ππ*, 11σσ* states were performed at the CASSCF(10/10)/aug(O)-AVTZ level—state averaging the specific state of interest with the ground state wavefunction for each fixed R0–H and allowing the rest of the nuclear framework to relax. CASPT2(10/10)/aug(O)-AVTZ single point energy calculations were then performed at these optimized geometries based on a fully SA-CASSCF wavefunction. Other excited states (i.e., the 21ππ*, 21σσ* states of the molecule and the A and B states of the phenoxyl radical) were also optimized to provide comparators with other experimentally determined values and to characterise the accuracy of the current \textit{ab initio} PESs in the vertical FC region and at R0–H = ∞. Equation of motion coupled cluster single and double excitations (EOM-CCSD) calculations were also performed at the optimized CASSCF ground state geometry with the same aug(O)-AVTZ basis to calculate the vectors of the transition dipole moments (TDMs) and associated oscillator strengths (f). All \textit{ab initio} calculations were performed in the MOLPRO program.\textsuperscript{22}

III. THEORY AND RESULTS

A. Symmetry and dynamics

We start by considering the prototypical case of phenol. The S0 and S1 states of phenol are planar, so the point group for both is C\textsubscript{3v}. In this point group, the symmetries of the three states of interest are 1A' (S0 and S1) and 1A'' (S2). As Fig. 1(a) shows, the S\textsubscript{1}(v = 0) level lies below the S1/S2 CI in energy, but above the H + phenoxyl(X\textsuperscript{2}B\textsubscript{1}) asymptote and the S2/S0 CI at extended R0–H. Non-adiabatic transitions between these states may thus be mediated by a' vibrational modes for S1\rightarrow S0, or by a'' modes for S1\rightarrow S2 and for S2\rightarrow S0. Such reasoning underpinned our earlier hypothesis that the population of levels with ν16a (a2/a') was odd in the planar (C\textsubscript{2v}) phenoxyl radicals, formed following excitation of the S\textsubscript{1}(v = 0) level of phenol-h3, was evidence for a dynamical pathway S1\rightarrow S0\rightarrow S2\rightarrow phenoxyl(X\textsuperscript{2}B\textsubscript{1}) + H with IC driving the first radiationless step.
However, the existence of two equivalent ground (and excited) state conformations of phenol results in a degeneracy, which is split when torsional tunnelling is taken into account. Each rovibronic level divides into two sub-levels with the same overall symmetry (\(a^\prime\) or \(a^\prime\prime\)) in \(C_n\). High resolution fluorescence spectra of phenol confirm the lifting of this degeneracy and reveal a ground state splitting of \(\sim 56\) MHz.\(^2\) As a consequence, the detailed structures and interpretation of both the infrared and ultraviolet spectra of phenol have necessitated reference to the non-rigid molecular symmetry group \(G_4\) (which is isomorphous with \(C_{2v}\)).\(^1\)

For the group \(G_4\), the electronic symmetries of the parent states of current interest are \(^1A_1\) (\(S_0\)), \(^1B_2\) (\(S_1\)), and \(^1B_1\) (\(S_2\)). The symmetries of the 30 parent normal modes of vibration that are retained in the phenoxyl radical are as for the parent molecule (in \(C_{2v}\)), while the symmetries of the three parent modes that disappear upon O–H bond fission are \(a_1\) (for the O–H stretch and bend) and \(b_1\) (the O–H torsion). Non-adiabatic transitions between the relevant electronic states could be mediated by \(b_2\) modes for \(S_1 \sim S_0\); by \(a_2\) modes for \(S_1 \sim S_2\); and by \(b_1\) modes for \(S_0 \sim S_2\). Thus the excitation of odd quanta of \(v_{16a}(a_2)\) is only compatible with the more direct \(S_1 \sim S_2\) \(\sim\) H + phenoxyl (\(X^2B_1\)) pathway, as proposed by Pino et al.\(^1\) despite the necessity of tunnelling through a large energy barrier under the \(^1B_2(S_1)/^1B_1(S_2)\) CI.

Such symmetry considerations invalidate our earlier hypothesis and the associated calculations.\(^9\),\(^18\),\(^20\),\(^23\) They also explain the lack of evidence of OH torsional (\(b_1\)) activity. This would appear to be in conflict with previous predictions, based on \textit{ab initio} calculation\(^7\) that OH torsion is the principal mode mediating dissociation via the \(S_1/S_2\) CI. But that calculation ignored the two-fold torsional degeneracy and used an asymmetric \(C_n\) point group. Within \(G_4\), the \(b_1\) torsional mode has two components separated by an angle of \(180^\circ\) and a high potential barrier. In calculating the \(\langle 1\pi\pi^*|H\pi\sigma^*\rangle\) matrix element for torsional coupling, the phases of these two components are such that they exactly cancel. (N.B. they reinforce each other at the lower \(S_0/S_2\) CI).

The greatest changes in vibrational wavenumber upon \(S_1 \sim S_0\) excitation in phenol are for \(v_4\) (358.3 \(\sim 685.9\) cm\(^{-1}\)), \(v_{16a}\) (187 \(\sim 408.5\) cm\(^{-1}\)), and for the OH torsion (634.7 \(\sim 309.2\) cm\(^{-1}\)). These are qualitatively consistent with the changes in bonding that accompany this excitation.\(^24\) For example, the C–O bond contracts from 1.369 to 1.326 Å, indicating an increase in double bond character and thus an increased barrier to O–H torsional motion. Within the phenyl ring, the C–C bonds all increase in length, by 0.059 Å (\(C_1-C_2\)), 0.050 Å (\(C_2-C_3\)), and 0.023 Å (\(C_3-C_4\)), thereby weakening the resistance to the internal ring twisting modes \(v_4(b_1)\) and \(v_{16a}(a_2)\). We have no knowledge of vibrational wavenumbers of phenol in its \(S_2\) state, because of the repulsion along \(R_{O-H}\). But this state correlates with the phenoxyl (\(X^2B_1\)) radical, for which \(v_4 = 647\) cm\(^{-1}\) and \(v_{16a} = 373\) cm\(^{-1}\) (i.e., similar to the values for the \(S_0\) state of phenol). There are only three \(a_2\) modes for phenoxyl \(X^2B_1\): \(v_{16a}\), \(v_{10a}\), and \(v_{17a}\). The latter two are predominantly C–H bending modes. Thus it is not surprising that \(v_{16a}\) appears to be the dominant coupling mode at the \(S_1/S_2\) CI; it is the only heavy framework motion of the appropriate symmetry to mix the relevant electronic wavefunctions. We now present dynamical calculations in justification of this new hypothesis.

Consider a two dimensional (2D) Hamiltonian in the \(R_{O-H}\) and \(q_{16a}\) displacement coordinates. The change in electronic symmetry \((^1B_2 \sim ^1B_1)\) will introduce a geometric phase effect as discussed previously for the dynamics at the lower CI.\(^23\) (The associated quantum interference around the \(S_1/S_2\) CI forces a change in symmetry to any outgoing vibronic wavefunction). The coupling matrix element \(H_{12}(q)\) between the \(S_1\) and \(S_2\) diabatic states must, therefore, be an odd function of \(q_{16a}\), and may be assumed to be linear in \(q_{16a}\), but to vary slowly with \(R_{O-H}\) over the interaction region. For \(q_{16a} = 0\), the two diabatic potentials can cross and there can be no transfer between the two states. Upon increasing \(q_{16a}\), however, there will be an avoided crossing resulting in an increasingly broad maximum along \(R_{O-H}\) for the lower adiabatic potential. The rate of tunnelling through this potential will show a near exponential dependence on the area under this maximum and above the total energy of approach (Fig. 2(a)). This
area will decrease with increasing $H_{12}$ and thus the rate will increase. We use a model system to explore these dynamics. This makes use of the new ab initio calculations of the relevant potentials along $R_{0-H}$, coupled with experimentally based harmonic potentials for $q_{16a}$, (see Sec. II above).

### B. Ab initio results

The PECs through $R_{0-H}$ presented here constitute some of the best calculations, in terms of size of basis set and active space, and available theoretical methods, yet reported for the excited states of phenol and for O–H bond cleavage in this molecule. With reference to Table I, the optimized excitation energies to the $S_1$, $S_2$, and $S_4$ states relative to $S_0$ are in good agreement with the available experimental data. The calculated energy of the (geometry optimized) $S_1$ state reported in Table I is $\sim 0.14$ eV below the experimental value, but has not had a zero-point energy (ZPE) correction applied to it. Another potential source of error could be from the imaginary level shift required to converge the CASPT2 calculations for all excited states. This (small) underestimation of the energy of the $S_1$ state can be expected to introduce some (predictable) errors in the “relaxed” PECs. From the perspective of the dynamical calculations (below) this error is likely to result in some over estimation of the area under the $\pi\pi^*$-type transition.

Table I. Comparison of calculated and experimentally derived transition energies and moments for phenol and the phenoxyl radical.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CASSCF(10/10)/aug(O)-AVTZ/</th>
<th>EOM-CCSD/aug(O)-AVTZ$^a$</th>
<th>Experimentally derived energy/eV</th>
<th>Previous calculated energies$^b$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>Vertical energy/eV Optimized energy/eV</td>
<td>Vertical energy/eV Oscillator Strength ($f$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta E(1^1\pi\pi^*\rightarrow S_0)$ [1$B_2$]</td>
<td>4.52</td>
<td>4.37</td>
<td>4.97</td>
<td>0.185</td>
</tr>
<tr>
<td>$\Delta E(1^1\pi\pi^*\rightarrow S_0)$ [1$B_1$]</td>
<td>5.64</td>
<td>5.47</td>
<td>5.67</td>
<td>0.001</td>
</tr>
<tr>
<td>$\Delta E(2^1\pi\pi^*\rightarrow S_0)$ [1$A_1$]</td>
<td>6.13</td>
<td>...</td>
<td>6.17</td>
<td>0.219</td>
</tr>
<tr>
<td>$\Delta E(2^1\pi\pi^*\rightarrow S_0)$ [1$A_2$]</td>
<td>6.59</td>
<td>6.57</td>
<td>6.18</td>
<td>0.029</td>
</tr>
<tr>
<td>$D_0$($H$–phenoxyl[$X^2B_1$])</td>
<td>4.31 (3.99)</td>
<td>4.05 (3.73)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Phenoxyl</td>
<td>$T_r(X^2B_2^r→X^2B_1)$</td>
<td>0.65</td>
<td>0.89</td>
<td>...</td>
</tr>
</tbody>
</table>
| $T_r(B^2A_2→X^2B_1)$ | 2.43 | 2.09 | ... | 2.08$^d$ / 2.03$^e$ | ... | ...

$^a$This study.
$^b$Calculated values in parenthesis indicate a zero point energy correction has been applied; square brackets denote that the previous study has optimized this energy.
$^c$Reference 11.
$^d$Reference 21.
$^e$Reference 32.
$^f$Reference 16: C22/aug-cc-pVDZ.
$^g$Reference 7: MRCI(8/8)/aug-cc-pVDZ.

The PECs through $R_{0-H}$ are fully bound along $q_{16a}$ for all $R_{0-H}$. In consequence the lower adiabatic cone is a small local peak along a rising potential ridge so that there is no possibility that any low energy path could avoid tunnelling en route to O–H dissociation. In this situation the tunnelling probability is zero for $q_{16a} = 0$, and the function of $H_{12}$ is to create a tunnelling probability that increases with increasing $q_{16a}$.

The EOM-CCSD transition dipole moments (TDMs) are superposed on the structures in Fig. 1(a) and listed in Table I. The $S_2$ transition is symmetric (which accounts for the small but non-zero oscillator strength predicted for the electric dipole forbidden (in $C_2$) $S_3$ transition). The $S_1$ TDM lies pseudo-parallel to the O–H bond; while that for the $S_3$ TDM transition is perpendicular to this bond, which has ramifications for the interpretation of the dissociation mechanism operating at $\lambda_{\text{phot}} < 248$ nm (Sec. III E).

### C. Dynamical calculations

Le Roy et al. have derived semi-classical methods for estimating the transmission probability through a 1D barrier and defined the linewidth $\Gamma$ as the ratio of the probability per vibrational cycle of transmission through the barrier ($T_R$) to the period of oscillation in the potential well.

$$\Gamma = (v_{\text{OH}}/2\pi) \ln(1 + \exp(2\pi \varepsilon)) \equiv v_{\text{OH}} T_R,$$

where $\varepsilon$ is an integral of the absolute wavevector between the inner (b) and outer (c) limits of the barrier (Fig. 2):

$$\varepsilon = -\frac{1}{\pi} \int_b^c |k(R)| dR,$$

with

$$k(R) = \sqrt{2(V_{ad}(R) - E_\gamma)/g_{\text{OH}}},$$
where $V_{ad}$ is the adiabatic potential curve, $E_v$ is the energy of the $S_1$ level of interest and $g_{OH}$ is the radial inertial constant.

The experimental Lorentzian linewidth of $\Gamma \approx 67$ MHz for levels contributing to the $S_1-S_0$ origin band, combined with $v_{OH} = 3582$ cm$^{-1}$, yields an experimental value of $T_R \leq 6 \times 10^{-7}$. Note that this is an upper limit, since the total linewidth includes major contributions from additional decay processes for the $S_1$ state (e.g., fluorescence, IC, ISC, etc.).$^{14,16}$

The unrelaxed ab initio (diabatic) potentials for the $S_1$ and $S_2$ states cross at $r_c = 1.21$ Å (Fig. 1(a)). The barrier below this has a maximum height $[V_{ad}(R_c) - E(S_1,\nu = 0)]$ of 5400 cm$^{-1}$, giving $k_{\text{max}} = 17.8$ Å$^{-1}$ and with a base width of 0.61 Å. This barrier leads to a calculated value of $T_R \sim 3 \times 10^{-7}$. This estimation of $T_R$ is the same order of magnitude as the experimental value, indicating that tunnelling is a plausible mechanism in the case. But it ignores the role of non-adiabatic coupling in promoting the transfer from $S_1$ to $S_2$. To address this issue we have carried out 2D wavepacket dynamics using a coupled diabatic basis.

The 2D wavepacket dynamics are based on the potential functions of Fig. 1(a) with $R_{O-H}$ as the dissociation coordinate, coupled with $q_{16a}$ as the promoting mode. The initial wavefunction $\chi^1(q_{16a}, R_{O-H})$ is restricted to the $S_1$ diabatic state and is the product of the lowest calculated eigenfunction of $V_1(R_{O-H})$ and an experimentally based harmonic $\nu = 0$ function of $q_{16a}$. Propagation is driven by coupling to the $S_2$ potential at the diabatic total energy, with $H_{12}(q_{16a}, R_{O-H})$ represented by $V_{12} \times q_{16a}$. A trial value for $V_{12}$ was optimized against the experimental $T_R$, resulting in $V_{12} = 2500$ cm$^{-1}$ radian$^{-1}$ (equivalent to $H_{12} = 220$ cm$^{-1}$ $\times q_{16a}$) and in a calculated $T_R = 3 \times 10^{-7}$. The amplitude of the ensuing outgoing wave in the exit channel, $\chi^2(q_{16a}, R_{O-H})$, is very low, and quickly reaches convergence for $R_{O-H}$ beyond the tunnelling region. The vibrational population distribution for the phenoxyl product is derived from exit channel correlation amplitudes in the usual way, leading to relative populations of 0.65, 0.26, 0.07, and 0.01 for product states with $v_{16a} = 1, 3, 5,$ and 7 (Fig. 3(c)).

As noted previously, the wavenumber of the $v_{16a}$ mode in the radical is approximately twice that for the $S_1$ state; the amplitude of this vibration is correspondingly reduced by a factor of approximately $\sqrt{2}$ upon dissociation. For comparison, a sudden F-C approximation, which maps $\chi^2(q_{16a}, R_{O-H})$ directly onto the $\chi^2$ basis at large $R_{O-H}$:

$$P^2 = \left( \int \chi^1_0(q_{16a}) |q_{16a}| \chi^2_0(q_{16a}) dq_{16a} \right)^2,$$

yields relative probabilities $P^2$ of 0.84, 0.14, 0.02, and 0.00 for forming product levels with $v_{16a} = 1, 3, 5,$ and 7, respectively (Fig. 3(b)). Thus a major cause of the extended odd $v$ population distribution derives from this large change in the active vibration frequency from $S_1$ to the radical. One notable feature of these results is that, although the calculated transmission probability varies strongly with changes in $V_{12}$, the relative populations do not.

The above calculation used ab initio potentials for $R_{O-H}$ stretching, with the rest of the nuclear framework fixed at the $S_0$ ground state geometry. The dynamical calculation was repeated with more justifiable “relaxed” potentials for which the geometry was optimized at each chosen value of $R_{O-H}$. This leads to $R_c = 1.21$ Å and a barrier with maximum height of 5100 cm$^{-1}$ and base width 0.52 Å. Relative to the unrelaxed potentials, the area under this barrier is decreased by 20% and $T_R$ is increased by 40% for the same value of $V_{12}$. More importantly, it leads to modified branching ratios of 0.74, 0.19, 0.06, 0.01 for $v_{16a} = 1, 3, 5,$ and 7 (Fig. 3(d)), which are closer to the FC values than with the unrelaxed potential. This is presumably a consequence of the narrower barrier width, which would reduce the 2D spreading of the outgoing wavepacket.

None of these calculated distributions (Fig. 3) give a perfect fit to the experimental data—which are themselves subject to significant error bars. However, the qualitative agreement between the 2D wavepacket calculations and the experimental data (Fig. 3(a)) lends strong support to the hypothesis that the dissociation of phenol $S_1(v = 0)$ molecules follows the $S_1 \rightarrow S_2 \rightarrow S_0 \rightarrow \text{phenoxyl}(X^2B_1)$ pathway, despite the necessity of tunnelling through the large energy barrier under the $S_1/S_2$ CI. Furthermore it also necessitates a re-assessment of the experimental data obtained when exciting phenol-$h_6$ through other $S_1$ vibrational levels, and when exciting deuterated and other substituted phenols. These latter issues are considered in the final sections of this paper.

D. Vibrationally excited phenol($S_1$)

There are many structured $S_1-S_0$ vibronic bands of phenol between 257 nm and the origin band at 275.113 nm which, when excited, yield H atoms from O–H bond fission. These involve a variety of vibrational modes and combination bands. We can envisage several types of decay mechanism accompanying $S_1 \rightarrow S_2$ tunnelling:

(i) Skeletal vibrations orthogonal to the dissociation coordinate with similar frequencies in $S_1$ and in the

![FIG. 3. Comparison between calculated and measured $v_{16a}$ population distributions formed by dissociation from the $S_1(v = 0)$ level of phenol-$h_6$. (a) Experimental data. (b) Sudden dynamic Franck-Condon calculation. (c) 2D wavepacket (unrelaxed potentials). (d) 2D wavepacket (relaxed potentials).](image-url)
the phenoxyl radical may act as spectator modes, carrying through in combination with the enabling $v_{16a}$ mode;

(ii) Given the long $S_1$ lifetime, higher energy modes may decay (by intramolecular vibrational redistribution (IVR)) into lower energy modes, which carry through in combination with an enabling mode, with the excess energy taken up by a disappearing mode (i.e., in eventual product translation);

(iii) Direct excitation to a disappearing mode may either lose that mode, with any other modes carrying through in combination, or

(iv) IVR may convert the disappearing mode to an active mode that carries through into the phenoxyl radical product.

All these mechanisms must preserve the overall vibronic symmetry, although it may be difficult to make unambiguous vibrational assignments where disappearing modes are suspected. Note that the use of the $G_4$ group rather than the $C_s$ group has necessitated revisions to the assignments for a few of our previously published spectra, as noted below.

Figure 4 presents some of the better resolved TKER spectra (plotted in terms of the internal energy, $E_{\text{int}}$, of the phenoxyl product) ordered by increasing energy of the excited $S_1$ level. We will discuss their assignments in the context of the previous paragraph.

The spectrum obtained following excitation via the $S_1,v=0$ level (Fig. 4(a)) shows not only the odd quantum progression in $v_{16a}$ but also the same progression of $v_{16a}$ in conjunction with $v_{18b}=1$ and 2. $v_{18b}$ is the CO in plane $b_2$ wagging mode, the appearance of which would, at first sight, appear to violate symmetry based expectations. However, the high kinetic energy of the departing H atom from the bent C–O–H moiety will be balanced by a strong recoil of the O atom along the $q_{18b}$ coordinate. A transient displacement of $\sim 10^\circ$ would carry enough energy to populate vibrational levels up to $v_{18b}=3$. Furthermore, this angular deflection will be symmetrised in combination with torsion ($\tau^{0^1}(a_1)$ and $\tau^{0^1}(b_2)$), with $v_{18b}$ behaving as a spectator to the disappearing torsional tunnelling ($b_2 \times b_3 = a_1$). Thus there is an $a_1$ component within the $G_4$ molecular group for both odd and even $v_{18b}$. $v_{18b}$ appears to one or more quanta in many of the TKER spectra observed following excitation to vibrationally excited $S_1$ levels.

The spectrum obtained when exciting via the hot-band $4_0^1 \tau^{0^1}_1$ (Fig. 4(b)) exhibits a sub-set of the same peaks in modes $v_{16a}$ and $v_{18b}$ as in Fig. 4(a), but with different relative intensities. The very existence of this particular vibronic transition suggests that there is some mixing of the $q_4$ and $q_6(b_1)$ modes. We also note that the frequency of the $v_4$ mode increases from 358 cm$^{-1}$ in the $S_1$ state to 647 cm$^{-1}$ in the phenoxyl radical ground state. We presume that this major frequency increase and possible mode mixing drives IVR to the disappearing $b_1$ torsional mode.

Excitation via $16a_2^1$ (Fig. 4(c)) again results in an odd quantum progression in product mode $v_{16a}$, though the maximum intensity is shifted to higher $v_{16a}$ in accord with FC expectations. But the $E_{\text{int}}$ spectrum also includes peaks for $v_{11} = 2$ or $v_{6a} = 1$ in conjunction with odd $v_{16a}$. $v_{11}$ is the lowest frequency $b_1$ mode, and $v_{6a}$ the lowest $a_1$ mode. Both of these are probably populated via IVR from the initially prepared $16a_2^1$ level. Excitation via $18b_0^1$ (Fig. 4(d)) results in analogous peaks to when exciting the $4_0^1 \tau^{0^1}_1$ transition (Fig. 4(b)), but with a more extended intensity distribution in $v_{18b}$ (as expected on FC grounds) and only one quantum of $v_{16a}$.

$6a_0^1$ (Fig. 4(e)) excites to the lowest $a_1$ mode. There is a weak peak at low internal energy consistent with forming radicals carrying one quantum of the enabling $v_{16a}$ mode, but which have lost the $v_{6a}$ quantum. Otherwise, the spectrum is essentially identical to that shown in Fig. 4(a), but shifted by

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**FIG. 4.** $E_{\text{int}}$ spectra of the phenoxyl products formed by photolysis of jet cooled phenol at $\lambda_{\text{phot}} =$ (a) 275.113 nm, (b) 274.735 nm, (c) 272.300 nm, (d) 272.145 nm, (e) 271.535 nm, (f) 267.903 nm. The $S_1$ vibrational level populated at each wavelength is indicated by the transition shown in the top right hand corner of each panel.
one quantum of $v_{16a}$ – which acts essentially as a spectator mode. This behaviour is repeated for $9a_{1}^{\pi}$ excitation (Fig. 4(f)). The TKER spectrum in this case shows a weak $v_{16a} = 1$ peak, but the main peaks indicate IVR from parent mode $v_{19a}$ (1150 cm$^{-1}$) to product mode $v_{1}$ (966 cm$^{-1}$) in conjunction with $v_{16a} = 1$ and the $v_{16b}$ progression of (Fig. 4(b)).

In summary, all these spectra indicate formation of phenoxyl radical products carrying at least one quantum in the enabling $v_{16a}(d_{2})$ mode (with population of higher (odd) $v_{16a}$ levels in some cases) and one or more quanta of $v_{16b}$. All these spectra conform to expectations based on the $G_4$ molecular symmetry group and the assumption of the $S_{1}(B_{2})\rightarrow S_{2}(B_{1})\rightarrow H +$ phenoxyl ($X^{2}B_{1}$) fragmentation pathway.

These assigned spectra explain why “fast” peaks in spectra obtained following excitation at $\lambda_{\text{phot}} \geq 248$ nm consistently appear in the TKER range $\sim 6000$–$7000$ cm$^{-1}$. Most of the vibronic structure of the $S_{1} \rightarrow S_{0}$ excitation involves modes orthogonal to $R_{O-H}$ and most of the associated vibrational excitation maps through into the radical as spectator motion and thus contributes little to the H atom tunnelling probability or the dissociation dynamics.

E. Excitation of phenol at $\lambda_{\text{phot}} < 248$ nm

The measured TKER spectra show a step change in appearance once $\lambda_{\text{phot}} \leq 248$ nm. The structure centred at TKER $\sim 6500$ cm$^{-1}$ has faded in intensity, and a new structured feature starts to appear at much higher TKER ($\sim 12000$ cm$^{-1}$). The recoil distribution of these fast H atoms is anisotropic, with a recoil anisotropy parameter $\beta \sim 0.5$. We have previously interpreted these features by assuming initial $S_{1} \rightarrow S_{0}$ excitation, with the outgoing flux accessing the $S_{2}$ PES at energies above the $S_{1}/S_{2}$ CI and dissociating promptly. Analysis of TKER spectra of this and related systems indicates that products are formed in progressions in $v_{16b}$ and $v_{19a}$ built on $v_{16b} = 1$.\cite{9, 21} We noted that $v_{16a}$ is an $a''$ mode in the $C_{6v}$ point group and presumed that the relative effectiveness of the various $a''$ modes that could enable $S_{1}(A') \rightarrow S_{2}(A'')$ coupling changes once there is no need for tunnelling under the CI. But we now recognize that this assignment violates the rules for the $G_{4}$ molecular symmetry group, since $v_{16b}$ is a $b_{1}$ mode, not an $a_{2}$ mode. Furthermore, this mechanism of initial $S_{1}$ population involves a TDM lying almost parallel to the dissociating O–H bond (see Fig. 1(a)), from which it is difficult to envisage preferential perpendicular recoil.

If excitation were directly to the $S_{2}$ state, it is not obvious why phenol($S_{2}$) molecules would not dissociate to $H +$ phenoxyl($X_{3}S_{0}$) products. It is important to note that transitions from the $S_{0}$ states of aromatic systems to $\pi\pi^{*}$ states are typically much weaker than those to $\pi\pi^{*}$ states and are often vibronically induced.\cite{28, 29} Our EOM-CCSD ab initio calculations (Table I) identify the $S_{3}(A'_{1})$ state lying close above the $S_{2}$ PES in the vertical FC region and predict a large TDM for this $S_{3} \rightarrow S_{0}$ excitation. Vibronically induced population of the $S_{2}$ state via intensity steering from the $S_{3}$ state requires mediation by a $b_{1}$ coupling mode, such as $v_{16b}$. We also note that the $a_{1}$ transition moment for the $S_{3}(A'_{1}) \rightarrow S_{0}$ excitation lies along the C–O bond (see Fig. 1(a)), so the measured recoil anisotropy ($\beta \sim 0.5$) is fully consistent with prompt dissociation along an axis close to that of the breaking O–H bond assuming an $S_{0}(A'_{1}) \rightarrow S_{2}(B'_{1}) \rightarrow H +$ phenoxyl ($X^{2}B_{1}$) pathway mediated by vibronic coupling from $S_{3}(A'_{1})$. Thus we deduce that, following direct excitation to the $S_{2}$ state, the $S_{1}/S_{2}$ CI plays no significant role in the production of fast $H +$ phenoxyl($X^{2}B_{1}$) radicals at $\lambda_{\text{phot}} \leq 248$ nm: though the observation\cite{21} of phenoxyl($X^{2}B_{2}$) products following excitation at $\lambda_{\text{phot}} \sim 230$ nm suggests that the $S_{2}/S_{0}$ CI at longer $R_{O-H}$ can exert some influence on the electronic branching in the radical products.

IV. IMPLICATIONS FOR RELATED SYSTEMS

A. Phenol-$d_{6}$ and phenol-$d_{5}$

Fully deuterated phenol-$d_{6}$ shows no measurable D atom yield following excitation to its $S_{1}(v = 0)$ level.\cite{9} Such a finding is consistent with the present dynamical calculations, which predict a rate of O–D bond fission by D atom tunnelling through the barrier under the $S_{1}/S_{2}$ CI $\sim 10^{3}$ times slower than that for H atom loss from phenol-$h_{6}$. D atom tunnelling is thus unlikely to compete with fluorescence and/or IC as a decay mechanism for phenol-$d_{6}(S_{1})$ molecules. Excitation at energies above the $S_{1}/S_{2}$ CI yields fast $D +$ phenoxyl-$d_{5}$ products, however, with a similar (albeit less structured) TKER distribution to that observed for the $H +$ phenoxyl-$h_{5}$ products from phenol-$h_{6}$ photolysis at $\lambda_{\text{phot}} \leq 248$ nm.\cite{9}

Replacing just the ring H atoms in phenol with D atoms (phenol-$d_{5}$) retains the O–H bond but reduces the calculated amplitude of motion in $q_{16a}$ by $\sim 10\%$ (and the wavenumber of $v_{16a}$ in the phenoxyl-$d_{5}$ products by $\sim 20\%$). Wavepacket calculations predict modest reductions in the probability of O–H bond fission by H atom tunnelling from the $S_{1}(v = 0)$ level (relative to that in phenol-$h_{5}$), and a slightly reduced partitioning into vibrational energy in the radical products. Experimentally, the H atom TOF spectrum following $S_{1}(v = 0) \rightarrow S_{0}$ excitation of phenol-$d_{5}$ (Fig. 5(a)) shows a clump of fast peaks dominated by a feature attributable to phenoxyl-$d_{5}$ products with $v_{16a} = 1$, but the population in levels with $v_{16a} = 3, 5$, etc., appears to be less than that predicted by the present modelling.\cite{21}

B. para-substituted phenols

Figure 4 has demonstrated a range of behaviours when exciting phenol-$h_{6}$ to $S_{1}$ levels with $\nu > 0$. Such selective vibrational energy disposal is not restricted solely to bare phenol. The $E_{\text{int}}$ spectrum of the 4-fluorophenoxyl fragments formed when exciting at the $S_{1} \rightarrow S_{0}$ origin of 4-fluorophenol is very similar to that of bare phenol (Fig. 5(b)), but with the addition of activity in modes $v_{18b}$ and $v_{19b}$ (an asymmetrically coupled C–F and C–O wagging motion)—both of which are understandable on dynamical FC grounds.\cite{18}

Introducing a methyl group to the phenol ring will increase the overall vibrational state density and thus the probability of IVR. Yet the vibrational energy disposal in the 4-methylphenoxyl fragments formed when exciting
4-methylphenol at its $S_1 \leftarrow S_0$ origin (Fig. 5(c)) is again dominated by a short progression in $v_{16a}$ = odd$^{19}$ and very reminiscent of that in the 4-fluorophenoxyl($\tilde{X}$) products from photolysis of 4-fluorophenol.

**C. Symmetry breaking substituted phenols**

Vibronic coupling between the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ excitations is driven by the vibrational moments of the orbital transition density $\pi^* \times \sigma^*$. The behaviour of substituted phenols which break the $G_4$ symmetry, but also dissociate by O–H fission, will depend on the extent to which both the $\pi^*$ and $\sigma^*$ LUMOs and the relevant vibrational modes remain localised on the phenyl ring with its OH group and also on any lowering of orbital symmetry such as mixing of $a_2$ and $b_1$ orbitals.

Figure 6 presents $E_{\text{int}}$ spectra of three asymmetrically substituted phenols which do dissociate by O–H bond fission. Figures 6(a) and 6(b) show, respectively, the spectra obtained following excitation of trans-ortho-methylphenol through a $S_1(3a_1) \leftarrow S_0$ methyl torsional transition and that from cis-meta-methylphenol when excited through its $S_1 \leftarrow S_0$ origin band.$^{20}$ Fluorescence lifetimes of these two methylphenols were cited by Pino et al.$^{16}$ in support of the $S_1 \rightarrow S_2$ tunnelling hypothesis. In both cases, the OH torsional degeneracy is sufficiently broken by cis- and trans- substitution to give separate isomers. Consequently the non-rigid $G_4$ molecular symmetry group is no longer appropriate and any symmetry constraints are those of the $C_s$ point group. Even so, both these spectra show a short progression in the $a''$ enabling mode equivalent to $v_{16a}$ of phenol ($v = 1, 3, 5$ in Fig. 6(a), $v = 1$ and $3$ in Fig. 6(b)), coupled with one or more $a'$ product modes. A significant feature of these enabling modes is that, as with $v_{16a}$ in phenol, their frequencies in the $S_1$ state are much lower than those in the eventual radical product.

Our final example, 4-hydroxyindole (Fig. 6(c)), is perhaps less intuitive since the molecule is less symmetric and the obvious chromophore is an indole. Huang et al.$^{30}$ suggested that the short fluorescence lifetime of 4-hydroxyindole in its $1L_b$ ($1\pi\pi^*$) state ($\tau_f = 0.18 \pm 0.1$ ns) is an indication of efficient keto-enol isomerisation in the excited state. However, excitation at the $1L_b \rightarrow S_0$ origin yields translationally excited H atom products. The deduced vibrational energy disposal in the radical co-fragment is once again reminiscent of that found for phenol-$h_6$, with population of levels involving (the equivalent of) $v_{16a} = 1, 3, 5$ along with a quantum of the $v_{18b}$ equivalent.$^{31}$

In almost all of the cases discussed in this paper, the enabling mode at the $S_1$/S2 CI reveals itself as a short (odd quantum only) progression in the corresponding vibrational mode of the radical product. In the case of bare phenol, this is explained in terms of the dynamic FC behaviour of a mode that...
has an $S_1$ frequency that is much lower than that in the radical product (and, by inference, in the $S_2$ state). This suggests that both the frequency difference and the vibronic coupling activity have a common electronic origin.

V. CONCLUSIONS

This paper revisits the dynamic mechanisms that underlie the UV photodissociation of phenol, and substituted phenols, in the light of symmetry restrictions arising from torsional tunnelling degeneracy. The potential function for the lowest repulsive state of prototypical phenol-$h\nu_0$, the $^1\pi\pi^*(S_2)$ state, has two CIs along the O–H stretching coordinate. Using the symmetry classifications of the non-rigid molecular symmetry group $G_4$, we show that only $a_2$ modes have the appropriate symmetry to enable vibronic coupling via the higher CI from the photo-prepared $^1\pi\pi^*(S_1)$ state to the dissociative $^1\pi\pi^*(S_2)$ PES and that only $b_1$ modes can promote coupling at the lower $S_0/S_2$ CI. The measured energy disposals in the phenoxyl products following excitation of higher vibrational levels of the $S_1$ state is also rationalised, in terms both of spectator modes and IVR between modes. These conclusions are shown to account for the specific product vibrational energy disposal observed for phenol and a range of substituted phenols, over a wide range of excitation energies. A common feature in many cases is the observation of a (odd quantum number only) progression in the mode which enables tunnelling under the $S_1/S_2$ CI, which we attribute to a FC contribution to a major change in vibration frequency. The present analyses serve to reinforce the hypothesis reached from recent correlations of the excited state lifetimes of phenol, and many substituted phenols, with the corresponding vertical energy gaps between their $S_1$ and $S_2$ PESs,\textsuperscript{16} which were used as evidence for O–H bond fission following tunnelling under the $S_1/S_2$ CI. Our previous discussion of the geometric phase effect at the $S_0/S_2$ CI\textsuperscript{23} applies equally to the symmetry change at the $S_1/S_2$ CI.

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\begin{thebibliography}{10}
\bibitem{17} The Wilson mode labelling notation provides a convenient way of highlighting the mapping between the parent (phenol) and radical (phenoxyl) modes of vibration and is used throughout.
\bibitem{22} MOLPRO, a package of \textit{ab initio} programs designed by H.-J. Werner and P. J. Knowles, version 2010, R. D. Amos, A. Bernhardsson, A. Berning, et al.
\bibitem{27} This is a reassignment of a previously published TKER spectrum for this excited level (Ref. 9). The peak at $E_{\text{TKER}} = 375$ cm$^{-1}$ was previously assigned to $v_{13} = 2$, which is essentially degenerate with $v_{16} = 1$.
\end{thebibliography}