Near-Ultraviolet Photodissociation of Thiophenol†

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H(D) Rydberg atom photofragment translational spectroscopy has been used to investigate the dynamics of H(D) atom loss C6H5SH(C6H5SD) following excitation at many wavelengths λphot in the range of 225—290 nm. The C6H5S cofragments are formed in both their ground (X2B1) and first excited (2B2) electronic states, in a distribution of vibrational levels that spreads and shifts to higher internal energies as λphot is reduced. Excitation at λphot > 275 nm populates levels of the first ππ* state, which decay by tunnelling to the dissociative 1πσ* state potential energy surface (PES). S—H torsional motion is identified as a coupling mode facilitating population transfer at the conical intersection (CI) between the diabatic 1ππ* and 1πσ* PESs. At shorter λphot, the 1πσ* state is deduced to be populated either directly or by efficient vibronic coupling from higher 1ππ* states. Flux evolving on the 1πσ* PES samples a second CI, at longer RSH, between the diabatic 1πσ* and ground (1ππ) PESs, where the electronic branching between ground and excited state C6H5S fragments is determined. The C6H5S(X2B1) and C6H5S(2B2) products are deduced to be formed in levels with, respectively, a' and a'' vibrational symmetry—behavior that reflects both Franck–Condon effects (both in the initial photoexcitation step and in the subsequent in-plane forces acting during dissociation) and the effects of the out-of-plane coupling mode(s), v11 and v18r, at the 1ππ*/1πσ CI. The vibrational state assignments enabled by the high-energy resolution of the present data allow new and improved estimations of the bond dissociation energies, D(0)(C6H5S—H) ≥ 28030 ± 100 cm⁻¹ and D(0)(C6H5S—D) ≤ 28610 ± 100 cm⁻¹, and of the energy separation between the X2B1 and 2B2 states of the C6H5S radical, ∆(0) = 2800 ± 40 cm⁻¹. Similarities, and differences, between the measured energy disposals accompanying UV photoinduced X—H (X = S, O) bond fission in thiophenol and phenol are discussed.

1. Introduction

Predictions by Sobolewski and Domcke† regarding dissociative excited electronic states of 1πσ* character in heteroaromatic molecules have fueled much recent interest in the photofragmentation behavior of these compounds.2 Ab initio studies reveal the potential energy surfaces (PESs) of these 1πσ* states to be repulsive in the X—H coordinate (where X is the heteroatom, for example, N, O, or, as here, S), leading to speculations regarding the possible importance of X—H fission in the nonradiative decay of these molecules following ultraviolet (UV) photoexcitation. Calculations3 on first-row heteroaromatic molecules (e.g., phenol, pyrrole, indole) indicate that, in each case, the 1πσ* states have 3s Rydberg character in the vertical Franck–Condon region and σ*-π*-antibonding valence character at extended Rπ—H. These 1πσ* electronic states also exhibit low oscillator strengths from the ground state and large dipole moments. In phenol, the diabatic 1πσ* PES was found to intersect both the bound, photofragment, diabatic 1ππ* state and the ground state in the O—H stretch coordinate. [For clarity, we use the terms 1πσ*, 1ππ*, 1πσ*, etc to label the diabatic states (and PESs) of interest, and reserve the descriptors σh, σl, etc for the corresponding adiabatic states and PESs.] These crossing points develop into conical intersections (CIs) with out-of-plane distortion of the nuclear framework.4

We have presented a detailed study of the H atom loss dynamics following UV photolysis of phenol at many wavelengths in the range of 200 ≤ λphot ≤ 280 nm² using the H atom photofragment translational spectroscopy (PTS) technique. The measured spectra provide information about the vibrational-state population distributions in the phenoxyl radical fragments formed upon O—H bond fission, which, in turn, provide insight into the nature of the coupling modes at the CIs between the 1πσ*/1ππ* and 1πσ*/1ππ PESs in the O—H dissociation coordinate. To investigate the effect of the heteroatom identity in such heteroaromatics and to explore the generality of X—H fission via 1πσ* states in second-row heteroaromatics, this article focuses on the H/D atom loss pathway following UV photodissociation of thiophenol-h1 and thiophenol-d1 (C6H5SH and C6H5SD), the sulfur analogue of phenol.

Experimental5 and theoretical6 investigations indicate that the ground-state equilibrium structure of thiophenol is planar, and microwave studies8 are consistent with a torsional barrier for rotation about the C—S bond of 270 cm⁻¹. An early PTS study9 investigated C—S bond fission in C6H5SH (following excitation at 193 nm) and derived a value for the relevant bond dissociation energy, D(0)(C6H5S—SH) = 365 ± 8 kJ mol⁻¹. Ion imaging studies of C6H5SH and (C6H5SD) photolysis at 243.1 nm revealed that the H/D fragments formed upon S—H(D) bond fission have bimodal translational energy distributions, attributable to thiophenoxyl radical formation in both the ground (2B2) and first excited (1B2) electronic states.10,11 Both dissociation channels exhibited anisotropic photofragment recoil velocity (v) distributions, with v preferentially aligned perpendicular to the laser polarization axis, indicating prompt dissociation, relative to the time scale of molecular rotation. These authors also noted that since these two states of C6H5S differ only in the relative orientation of the singly occupied 3pπ orbital localized on the sulfur (parallel or perpendicular to the molecular plane), UV...
photolysis of C₆H₅SH represents a route to achieving intramolecular orbital alignment within this radical. In this article, we present a detailed study of the H/D atom loss pathway from C₆H₅SH/C₆H₅SD following photolysis at many wavelengths within the range of 225 ≤ λ_{phot} ≤ 290 nm. We also present complementary “action spectra” for forming H/D atoms, (monitored as H⁺/D⁺ ions) as a function of λ_{phot}. The long-wavelength onset for H/D atom formation coincides with the onset of parent absorption at ~290 nm, which we assign to the S¹ – S₀(ππ → π) origin. A weak, structured, resonance-enhanced multiphoton ionization (REMPI) spectrum of the parent ion was also recorded. The long-wavelength onset of this spectrum was found to lie at slightly higher energy than the 1ππ(ππ → π) origin; this we interpret in terms of absorption to, and subsequent ionization from, a longer lived triplet state.

The present H atom TOF spectra confirm the previous findings regarding thiophenoxyl radical formation in both the ground and first excited electronic states, even at the long-wavelength absorption limit (~290 nm). Structure present in the TOF spectra indicates that these radicals are formed in a select subset of the available vibrational levels, the assignments of which provide detailed insights into the fragmentation mechanisms. Polarization dependence studies reveal that photolysis at λ_{phot} > 275 nm results in an isotropic distribution of radical recoil velocities, whereas at shorter wavelengths, the fastest fragments are formed with perpendicular recoil anisotropy. Comparison between H and D atom TOF spectra obtained following photolysis of C₆H₅SH and C₆H₅SD reveals contributions from rival C–H bond fission processes to the measured photofragment yield at a given λ_{phot}, while comparisons between the present data and that reported recently for the related heteroaromatic system, phenol, and the 4-halophenols serve to highlight similarities and differences in the relative activities of different coupling modes at the CIs sampled en route to dissociation that are revealed in the eventual product state distributions.

2. Experimental Section

The experimental setup for the H/D (Rydberg) atom PTS studies has been described previously. Thiophenol (C₆H₅SH) was obtained commercially (Acros Organics, ≥99% purity), and its vapor pressure (~2 Torr) seeded in argon backing gas (~700 Torr) was expanded into vacuum through a pulsed valve (General Valve Series 9). Thiophenol-d₅ (C₆H₅SD) was prepared by mixing C₆H₅SH (5 ml) with excess D₂O and shaking vigorously. The resulting C₆H₅SD was vacuum distilled into a glass bulb, which was subsequently filled with argon to a total pressure of 700 Torr, and the gas mixture was admitted to the vacuum system as described above.

Photolysis radiation was provided by the second-harmonic output of a Nd-YAG pumped dye laser (Spectra Physics GCR-270 plus PDL-2), which yielded UV pulse energies in the range of 0.5–3 mJ. This radiation was focused into the interaction region with a 75 cm focal length lens. The wavelength of the dye laser radiation was established by directing a fraction of the Nd-YAG laser fundamental output and then focussing the resulting linearly polarized 364.7 nm radiation into a phase-matched Kr/Ar mixture. The Lyman-α radiation so derived was then refocused (MgF₂ lens) into the interaction volume situated 57 cm beyond the end of the tripling gas cell. The λ = 366 nm photons required for the second step of the double-resonant excitation scheme were obtained by frequency doubling (in a DCDCA crystal) 732 nm dye laser radiation.

The composition of the molecular beam was investigated by resonance-enhanced multiphoton ionization (REMPI) in the source region of a (removable) TOF mass spectrometer within the apparatus. REMPI spectra were obtained by scanning the photolysis laser in the range of 225 ≤ λ_{phot} ≤ 295 nm, monitoring the yield of parent (m/z 110) ions. Introducing Lyman-α radiation and the 364.7 nm UV fundamental from which it is derived allowed measurement of action spectra for forming H/D atoms (detected as H⁺/D⁺ ions following (1+1’) resonance-enhanced threshold ionization).

The length of the TOF axis used in these experiments (d = 370–371 mm) was frequently recalibrated by recording TOF spectra of H/D atoms resulting from H₂S/D₂S photolysis at 225 ≤ λ_{phot} ≤ 290 nm, monitoring the yield of parent (m/z 110) ions. Introducing Lyman-α radiation and the 364.7 nm UV fundamental from which it is derived allowed measurement of action spectra for forming H/D atoms (detected as H⁺/D⁺ ions following (1+1’) resonance-enhanced threshold ionization).

The Lyman-α wavelength (λ ≈ 121.6 nm, ν = 82259 cm⁻¹ (H₂)) [v = 82280 cm⁻¹ (D₂)] and at λ ~ 366 nm were provided by two dye lasers pumped by a single Nd-YAG laser (Continuum Powerlite 9010). The Lyman-α radiation was generated by mixing the appropriate dye laser output with residual 1064 nm Nd-YAG laser fundamental output and then focussing the resulting linearly polarized 364.7 nm radiation into a phase-matched Kr/Ar mixture. The Lyman-α radiation so derived was then refocused (MgF₂ lens) into the interaction volume situated 57 cm beyond the end of the tripling gas cell. The λ = 366 nm photons required for the second step of the double-resonant excitation scheme were obtained by frequency doubling (in a DCDCA crystal) 732 nm dye laser radiation.

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The ionization potential of thiophenol (8.30 eV18) lies below the two-photon energy at this wavelength, yet minimal parent (m/z 110) ion signal was observed when exciting at any λ_{phot} > 284 nm. As Figure 2a shows, a weak, structured parent ion spectrum with origin at λ_{phot} = 282.975 nm (ν₀₀ = 35339 cm⁻¹) was observed, however. The parent ion yield declined as λ_{phot} was reduced further, and by λ_{phot} = 265 nm, little photolysis-laser-dependent m/z 110 ion yield was observ-
The temperature of the result of 1 electronic state. This parent ion yield is presumed to arise as a beam expansion. The first torsional mode should cool so inefficiently in our molecular UV photolysis of C6H5SD. The inset in (a) shows the calculated pattern ∆ of ground- and excited-state torsional levels and the associated with torsional transitions of the S1 level in the S0 state. The separations between the sharp peaks near this origin are ∼40 cm⁻¹. Such small peak spacings are most plausibly associated with torsional transitions of the S−H rotor. Calculations employing model V2 torsional potentials with respective barrier heights of 300 cm⁻¹ for the S0 state (cf. an experimental estimate of ∼267 cm⁻¹ (ref 8)) and 590 cm⁻¹ for the excited state (illustrated in the inset to Figure 2a) reproduce the observed structure satisfactorily and show that these features are associated with ∆τS−H = 0 transitions from ground-state levels, with τS−H = 0, 1, 2, 3, ... The calculations succeed in reproducing the evident splitting of the fourth peak (attributable to tunneling splitting of the 3a1 and 3a2 torsional components of the τS−H = 3 level in the S0 state) but require the assumption of a torsional temperature of ∼300 K within the S0 state in order to replicate the observed intensity distribution. It is currently unclear why this torsional mode should cool so inefficiently in our molecular beam expansion. The first (τ1) member of the corresponding torsional progression was observed, weakly, in the action spectra for forming both parent ions and H atom products in previous studies of phenol in this same apparatus, but the torsional level spacing in that case is much larger (τ0−τ1 = 309 cm⁻¹). A room-temperature Boltzmann distribution over the deduced torsional levels of C6H5SH(S0) yields an average internal energy of ⟨Eint(C6H5SH)⟩ ≈ 100 cm⁻¹. The structure evident in the range of 281 < λphoton < 282.975 nm repeats at higher wavenumbers, most notably at ν00 + 372 cm⁻¹, ν00 + 682 cm⁻¹, and ν00 + 946 cm⁻¹. This we attribute to analogous torsional progressions, built off of different vibrational levels within the excited electronic state. This parent ion yield is presumed to arise as a result of 1 + 1 REMPI via a relatively long-lived state with small oscillator strength, possibly a triplet state. Similar studies of the C6H5SD isotopologue failed to identify any corresponding wavelength-dependent parent ion yield.

The Lyman-α radiation (together with the 364.7 nm precursor radiation from which it is derived) alone also yielded a weak parent (m/z 110) ion signal but negligible H⁺ or other parent ion fragmentation products. However, TOF-MS recorded with both the photolysis and Lyman-α pulses present, with the latter delayed by ∼10 ns, showed a dominant H⁺ ion signal. Two-color excitation spectra for forming H⁺/D⁺ ions from C6H5SH/C6H5SD were recorded across the range of 240 ≤ λphoton ≤ 295 nm. As shown in Figure 2b and c, both spectra exhibit a number of broad features and very similar long-wavelength onsets for H/D atom formation. The action spectrum for forming D atom products is more structured, but in both cases, the structure (though not the yield) disappears once λphoton < 265 nm. These action spectra match well with the previously reported onset of UV absorption and are assigned in terms of excitation to (various vibrational levels of) the S1 state that dissociates to yield H/D atoms amongst the dissociation products. Torsional structure analogous to that observed in the parent C6H5SH⁺ two-photon ionization spectrum (Figure 2a) can be expected to accompany each vibrational band in the S1−S0 spectrum, which will contribute to the breadths of the individual features in the action spectra for forming H/D atom photoproduets. Given a similar pattern of torsional fine structure to that in Figure 2a, the breadth of the S1−S0 origin in C6H5SH (centred at λphoton = 285.8 nm) can be reproduced by ascribing Lorentzian widths to the individual features, consistent with an excited-state lifetime of ∼130 fs. This short excited-state lifetime presumably accounts for the non-observation of these broad S1−S0 features in the one-color spectrum for forming parent ions.

### 3.2. Ab Initio Calculations

Ab initio calculations using time-dependent density functional theory (TD-DFT) with the HCTH(407) exchange correlation functional were undertaken to ascertain the excited electronic states of C6H5SH that might be important in the wavelength range of interest. The ground-state geometry was optimized at the DFT HCTH/6-311G+++(d,p) level. Vertical excitation energies calculated with TD-DFT at this geometry, using the same functional and basis set, are listed in Table 1. These studies confirm that the highest occupied molecular orbital in the ground state is dominated by a nonbonding 3πσ orbital localized on sulfur and predict that the S1(π* − π) state lies at an energy of 4.36 eV, in good agreement with the onsets of both UV absorption (Figure 1) and H atom formation. However, TOF-MS recorded with both the photolysis and Lyman-α pulses present, with the latter delayed by ∼10 ns, showed a dominant H⁺ ion signal. Two-color excitation spectra for forming H⁺/D⁺ ions from C6H5SH/C6H5SD were recorded across the range of 240 ≤ λphoton ≤ 295 nm. As shown in Figure 2b and c, both spectra exhibit a number of broad features and very similar long-wavelength onsets for H/D atom formation. The action spectrum for forming D atom products is more structured, but in both cases, the structure (though not the yield) disappears once λphoton < 265 nm. These action spectra match well with the previously reported onset of UV absorption and are assigned in terms of excitation to (various vibrational levels of) the S1 state that dissociates to yield H/D atoms amongst the dissociation products. Torsional structure analogous to that observed in the parent C6H5SH⁺ two-photon ionization spectrum (Figure 2a) can be expected to accompany each vibrational band in the S1−S0 spectrum, which will contribute to the breadths of the individual features in the action spectra for forming H/D atom photoproduets. Given a similar pattern of torsional fine structure to that in Figure 2a, the breadth of the S1−S0 origin in C6H5SH (centred at λphoton = 285.8 nm) can be reproduced by ascribing Lorentzian widths to the individual features, consistent with an excited-state lifetime of ∼130 fs. This short excited-state lifetime presumably accounts for the non-observation of these broad S1−S0 features in the one-color spectrum for forming parent ions.

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bond fission in phenols. The S₃(1c) state, which is displayed in Figure 3. Following the convention to ground-state C₆H₅S(X₂B₁) diabatic states. The PES of the S₃(1c) state is shown in Figure 2a. The vertical transition to the S₃(1c) state is predicted at 4.52 eV. The antibonding orbital is largely localized on the S–H bond, suggesting that this state is likely to be repulsive in the S–H stretch coordinate and identifying this state as the analogue of the 1πσ* state implicated in O₂ dissociation limits. The S₃(1c) state was found to lie ∼4.9 eV and to have a large oscillator strength, in good accord with the marked increase in parent absorption at λ ∼ 250 nm (see Figure 1).

These findings agree well with the results of higher-level electronic structure calculations reported by Lim et al. These confirm that the ground state of C₆H₅SH correlates diabatically with the excited C₆H₅S(²B₂) state of the radical and that the 1πσ* state is indeed dissociative in the C₆H₅SH/CH₃SD at many wavelengths within the range of 225 ≤ λₚhot ≤ 290 nm. Consistent with the studies of Lim et al., the fast H/D atoms are deduced to arise via S–H/D bond fission, generating C₆H₅S radicals as the cofragments. The measured TOF data are converted to total kinetic energy release (TKER) spectra using the relation

\[ TKER = \frac{1}{2} \left( \frac{m_{HD}}{m_{HD}} + \frac{m_{H}}{m_{H}} \right) \left( \frac{d}{t} \right)^2 \]  

where \( m_{HD} \) and \( m_{H} \) are the mass of the H/D atom (\( m_{H} = 0.0179 \) u/amu = 2.0141 u) and the partner fragment (\( m_{H} = 109.17 \) u), respectively, \( d \) is the distance separating the interaction volume and the center of the front face of the detector, and \( t \) is the measured H/D atom TOF. Intensity "re-binning" required use of the appropriate \( r^2 \) Jacobian for converting such TOF data into TKER space.

Figure 3 shows illustrative H atom TOF spectra recorded following photodissociation of C₆H₅SH/CH₃SD at many wavelengths within the range of 225 ≤ λₚhot ≤ 290 nm. Consistent with the present work, TOF data are converted to total kinetic energy release (TKER) spectra using the relation

\[ TKER = \frac{1}{2} \left( \frac{m_{HD}}{m_{HD}} + \frac{m_{H}}{m_{H}} \right) \left( \frac{d}{t} \right)^2 \]  

where \( m_{HD} \) and \( m_{H} \) are the mass of the H/D atom (\( m_{H} = 0.0179 \) u/amu = 2.0141 u) and the partner fragment (\( m_{H} = 109.17 \) u), respectively, \( d \) is the distance separating the interaction volume and the center of the front face of the detector, and \( t \) is the measured H/D atom TOF. Intensity "re-binning" required use of the appropriate \( r^2 \) Jacobian for converting such TOF data into TKER space.
serve to confirm the planarity of the radical in both electronic states, are listed in Appendix 1. Vibrational wavenumbers for the C₆H₅SH parent molecule in its ground state, calculated at the same level of theory, are in good agreement with experimental values, encouraging confidence in the reliability of the predicted radical wavenumbers. The Wilson mode numbering scheme is used throughout since it is insensitive to the loss of the three S–H modes and thus serves to illustrate the complementarity of the ring vibrations in the parent and radical products. The relative peak intensities in the TKER spectra reflect the branching ratios for forming C₆H₅S products in specific electronic (X₂B₁/2B₂) and vibrational (v) states, while the widths of the peaks indicate that the radical products are formed with relatively little rotational excitation. As Figure 4c shows, an unstructured feature becomes increasingly evident at low TKER as λₚhot is reduced. The TKER of this broad feature, which is centred at ~2300 cm⁻¹ (~3300 cm⁻¹ in the case of D atoms from photolysis of C₆H₅SD), is largely insensitive to λₚhot. Such observations are very reminiscent of similar broad features observed in the TKER spectra derived from H atom TOF spectra in many other heteroaromatics, for example, phenol, and as in those cases, we attribute this signal to “statistical” unimolecular decay of highly vibrationally excited parent molecules formed by radiationless transfer following one- (and multi-) photon excitation. The detailed forms of the measured TKER spectra evolve with λₚhot. These trends, and their interpretation, are presented below in a number of subsections partitioned to assist the reader.

### 3.3.1. Photodissociation at Long Wavelengths, λₚhot > 275 nm

**Overview and Dₒ(C₆H₅S–H).** The action spectra for forming H/D atom products at these wavelengths are structured (Figure 2). As Figure 5 shows, the TKER spectra obtained from H atom TOF spectra recorded in this wavelength range also show the most clearly resolved structure, but polarization studies reveal that the distribution of fragment recoil velocities is isotropic. λₚhot = 290.00 nm is the longest wavelength at which H atom formation is observed. Analysis of the TKER spectra obtained at this ((Figure 5a) and neighboring wavelengths allows determination of the S–H bond strength, Dₒ(C₆H₅S–H), via the relationship

$$ Dₒ(C₆H₅S–H) = Eₚhot + Eₚ(C₆H₅SH) - TKER - Eₚ(C₆H₅S) $$

where Eₚ(C₆H₅SH) and Eₚ(C₆H₅S) are, respectively, the internal energies of the S₀ parent molecule and of the C₆H₅S photoprocess. Our analysis of the parent excitation spectrum (Figure 2a) implies a mean value of $⟨Eₚ(C₆H₅SH)⟩$ ~ 100 cm⁻¹, associated with the appreciable population of torsional levels with $τ_{S–H}$ > 0. Since the H atoms of interest arise via S–H bond fission, this $Eₚ(C₆H₅SH)$ cannot be retained in the dissociation; it will be largely converted into TKER, with a small partitioning into framework rotation. The nonzero $Eₚ(C₆H₅S)$ thus contributes a ~100 cm⁻¹ shift in the TKER spectra, while the spread of possible $Eₚ(C₆H₅SH)$ (associated with the photodissociation of parent molecules with $τ_{S–H}$ = 0, 1, 2, etc.) serves to broaden the observed TKER peaks.

As will be demonstrated below, the peak at the highest TKER in spectra such as that obtained at λₚhot = 290.00 nm is most plausibly assigned to formation of H + C₆H₅S(X²B₁, ν = 0)
products (i.e., products with $E_{\text{int}}(C_6H_5S) = 0$). Given this assignment, and assuming $\langle E_{\text{int}}(C_6H_5SH) \rangle = 100 \text{ cm}^{-1}$, eq 2 yields $D_D(C_6H_5S-H) = 28030 \pm 100 \text{ cm}^{-1}$ (335.3 ± 1.2 kJ mol$^{-1}$). As discussed below, this value should be regarded as an upper limit since we cannot definitively exclude the possibility that all of the products carry an additional (unrecognized) quantum of vibration. A similar analysis of the (less well resolved) TKER spectra of C6H5SD at $\lambda_{\text{phot}} = (a) 285.80$, (b) 282.80, (c) 280.245, (d) 278.272, (e) 277.161, and (f) 274.421 nm, recorded with $\lambda_{\text{phot}}$ aligned at $\theta = 90^\circ$ to the TOF axis. The assignments have been positioned using the ab initio anharmonic wavenumbers listed in Appendix 1.

Figure 6. Internal energy spectra of C6H5S radicals formed following excitation of C6H5SD at $\lambda_{\text{phot}} = (a) 285.80$, (b) 282.80, (c) 280.245, (d) 278.272, (e) 277.161, and (f) 274.421 nm, recorded with $\lambda_{\text{phot}}$ aligned at $\theta = 90^\circ$ to the TOF axis. The assignments have been positioned using the ab initio anharmonic wavenumbers listed in Appendix 1.

Figure 7. Illustrations of the nuclear motions associated with active vibrational modes identified in the C6H5S products arising in the long-wavelength photolysis of C6H5SH and C6H5SD: (a–c) show the in-plane vibrations induced by dynamic (dFC) or vertical (vFC) Franck–Condon effects, (d) and (e) show the modes induced by dynamics at the conical intersection, and (f) shows the C–S wagging vibration, $v_{18s}$, induced impulsively during the dissociation.

corresponding spectra obtained by monitoring D atom loss following excitation of C6H5SD in this same long-wavelength range (Figure 6). Peak assignments, based on the calculated vibrational wavenumbers listed in Appendix 1, are shown above the relevant spectra in these figures. Each spectrum shows a number of characteristic features, which are now reviewed.

Energy Disposal and Product Mode Assignments. Consider the $\lambda_{\text{phot}} = 290.00$ nm data shown in Figure 5a. The peak separations in the low $E_{\text{int}}(C_6H_5S)$ region are noticeably wider than those at higher internal energy. The former structure can be assigned in terms of formation of ground-state C6H5S(X2B1) radicals in their $v = 0$ level and in levels carrying one or two quanta of excitation in modes $v_{18s}$ (the in-plane C–S wag) and $v_{16s}$ (a symmetric ring breathing mode). For future reference, the nuclear motions associated with these and other modes, introduced subsequently, are displayed in Figure 7. The set of peaks beginning at $E_{\text{int}}(C_6H_5S) = 2960 \text{ cm}^{-1}$ is assigned to the C6H5S(B2)+ H product channel. However, the spacings between these peaks cannot be assigned using the vibrational wavenumbers listed in Appendix 1 if the 2960 cm$^{-1}$ peak is assigned to C6H5S(B2, $v = 0$) products. These, and the companion peaks in all spectra displayed in Figures 5 and 6, can only be assigned consistently if the 2960 cm$^{-1}$ feature is associated with formation of C6H5S(B2) radicals with one quantum of excitation in the lowest-frequency $a''$ mode ($v_{11}$, a ring-puckering vibration with $b_1(C_2)$ symmetry). The peak at $E_{\text{int}}(C_6H_5S) = 3215 \text{ cm}^{-1}$ can then be assigned to C6H5S(B2) products carrying a quantum of $v_{16s}$ (another low-frequency $a''$ ring-puckering mode of $a_2$ symmetry in C2v). The peaks at $E_{\text{int}}(C_6H_5S) = 3420$ and at $\sim 4090 \text{ cm}^{-1}$ are consistent with formation of C6H5S(B2) radicals carrying one quantum of $v_{11}$ together with, respectively, a quantum of $v_{29}$ or $v_{15}$ (both of which are in-plane ring breathing modes). Significantly, these assignments imply that all modes active in the C6H5S(B2) products have $a'$ vibrational symmetry, whereas the populated levels of the C6H5S(B2) products all have $a''$ vibrational symmetry. Given these assignments, the energy difference between the electronic origins of the X2B1 and B2 states of the thiophenoxyl radical is determined as $T_0 = 2800 \pm 40 \text{ cm}^{-1}$, in reasonable accord with a recent theoretical estimate (2674 cm$^{-1}$ (ref 11)).

Given $D_D(C_6H_5S-H)$, eq 2 can be rearranged so that TKER spectra can be replotted on a common $E_{\text{int}}(C_6H_5S)$ internal energy scale, which is independent of $\lambda_{\text{phot}}$ and aids assignment of the vibrational energy disposal within these products. The spectra displayed in Figure 5 are plotted in this way, as are the
The spectrum obtained at $\lambda_{\text{phot}} = 285.80$ nm (Figure 5b) is very similar, though the branching into levels carrying a quantum of $v_{6a}$ is enhanced in both product channels and additional peaks appear that are attributable to the population of levels carrying a quantum of $v_1$ (another symmetric ring breathing mode; see Figure 7). The $\lambda_{\text{phot}} = 282.80$ nm spectrum (Figure 5c), obtained following excitation at the maximum of the second peak in the action spectrum for forming H atom products (Figure 2b), again shows some similarities but also noteworthy differences. The relative yield of C$_6$H$_5$S(X$^2B_1$, $v = 0$) radicals is much reduced, but new features attributable to the population of levels with $v_{6a} \geq 2$ appear (particularly in the C$_6$H$_5$S(B$^2$) product channel), suggesting that $v_{6a}$ may be active in the S$_1 \rightarrow$ S$_0$ excitation at this wavelength. Similar behavior (albeit involving different in-plane modes) is observed at $\lambda_{\text{phot}} = 277.50$ and 275.00 nm, resonant with further weak peaks in the action spectrum for forming H atom products. The strongest features in the former spectrum (Figure 5d) indicate population of levels involving $v_{15} = 1$ (alone in the case of the X$^2B_1$ products and in combination with $v_{11} = 1$ in the case of C$_6$H$_5$S(B$^2$)), whereas peaks attributable to population of combination levels with excitation in both $v_{15}$ and $v_{6a}$ are clearly evident in the $\lambda_{\text{phot}} = 275.00$ nm spectrum (Figure 5e).

As Figure 6 shows, similar trends are found in the $E_{\text{end}}$(C$_6$H$_5$S) spectra obtained following long-wavelength photolysis of C$_6$H$_5$SD. The data obtained at $\lambda_{\text{phot}} = 285.80$ and 282.80 nm (Figure 6a and b), following excitation at the centers of the first two broad features in the action spectrum for forming D atoms (Figure 2c) reveal $E_{\text{end}}$(C$_6$H$_5$S) distributions similar to, though less well resolved than, those seen in the analogous C$_6$H$_5$SH studies (Figure 5b and c). As in that case, the structure is interpretable in terms of the population of levels involving $v_{6a}$ and $v_{11}$ (in combination with the out-of-plane mode $v_{11}$ in the case of the B$^2$ products). The poorer resolution of these TKER spectra is most probably a reflection of increased rotational excitation of the C$_6$H$_5$S product as a result of the greater impulse accompanying S–D bond fission. Similar trends have been noted when comparing peak shapes in TKER spectra of the H + pyrrolyl and D + pyryrol-d$_3$ products resulting from UV photolysis of pyrrole and pyrrole-d$_3$.

Moving to shorter $\lambda_{\text{phot}}$, weak features indicative of population in product modes involving quanta of $v_{12}$ (at $\lambda_{\text{phot}} = 280.245$ nm, Figure 6c), $v_1$ (at $\lambda_{\text{phot}} = 278.272$ nm, Figure 6d), $v_{15}$ (at $\lambda_{\text{phot}} = 277.161$ nm, Figure 6e), and the combination mode $v_{15} + v_{6a}$ (at $\lambda_{\text{phot}} = 274.421$ nm, Figure 6f) are recognizable as is the general trend for the population distribution within both product channels to shift to higher internal energy.

Several of the foregoing observations have clear parallels with previous findings regarding the photofragmentation of phenol following excitation near its S$_1$–S$_0$ origin. The finding that the H(D) atoms formed at these long wavelengths have isotropic recoil velocity distributions suggests that the dissociation time scale is longer than the rotational period of the excited-state molecule. Such an observation is consistent with the assumption that the initial absorption is to the $1\pi\sigma^*$ (S$_1$) state. Reference to Figure 3 suggests that subsequent S–H(D) bond fission must involve radiationless transfer to the $1\pi\sigma^*$ PES, either directly by tunnelling from S$_1$ or possibly, as in the case of phenol, via internal conversion to high vibrational levels of the $1\pi\pi$ state and subsequent transfer at the long-range CI between the diabatic $1\pi\sigma^*$ and $1\pi\pi$ PESs. The foregoing product vibrational state assignments provide further insights into the dissociation dynamics.

Symmetry Considerations. The S$_1$ (and S$_0$) states of the parent molecule have $\Lambda'$ electronic symmetry, whereas the $1\pi\pi^*$ state has $\Lambda''$ electronic symmetry. The X$^2B_1$ state of the C$_6$H$_5$S radical transforms as $\Lambda''$ in the C$_1$ point group of the parent, while the B$^2$ excited state of the radical has $\Lambda'$ symmetry. Experimentally, we observe population of $\Lambda'$ vibrational levels of the X$^2B_1$ state product and $\Lambda''$ vibrational levels of the B$^2$ state radical, that is, all identified product levels have $\Lambda''$ vibronic symmetry. Consider parent excitation at the S$_1$–S$_0$ origin. Both $\nu = 0$ levels have $\Lambda'$ vibrational (and $\Lambda''$ vibronic) symmetry. Indeed, Franck–Condon arguments require that any S$_1$ level populated by excitation from the S$_0(\nu = 0)$ level should have $\Lambda'$ vibronic symmetry. (As noted previously, a significant fraction of the C$_6$H$_5$SH(C$_6$H$_5$SD) sample in the present experiments is in levels with $\nu_5 - \nu_1 = 0$; therefore, the ensemble of photoexcited molecules is likely to contain states of both $\Lambda'$ and $\Lambda''$ vibronic symmetry.) Overall vibronic symmetry must be conserved in the subsequent evolution to dissociation products. On this basis, products with $\Lambda'$ vibronic symmetry might have been expected, contrary to observation. This apparent dichotomy can be resolved, however, if we assume that coupling between the diabatic $1\pi\pi^*$ and $1\pi\sigma^*$ PESs is mediated by S–H torsion (an $a''$ mode). Transfer of flux from an $1\pi\sigma^*$ level of $\Lambda'(\Lambda'')$ vibronic symmetry would thus result in population of $\pi\pi^*$ levels carrying an odd(even) number of quanta in $\nu_5 - \nu_1$. Motion in this mode must “soften” upon S–H extension, however, and eventually be lost as product translation (and/or framework rotation). As mentioned previously, we recognize the possibility that all of the observed product states might carry an additional quantum of vibration in another $a''$ mode arising as a result of the $1\pi\pi^*/1\pi\sigma^*$ coupling, as observed in the case of phenol photolysis at $\lambda_{\text{phot}} < 246$ nm, where all phenoxyl fragments are deduced to carry a quantum of $\nu_{10b}$. Unfortunately, these two possibilities are not distinguishable in the present experiments; the consequence of the alternative interpretation (and the resulting offset of the implied $E_{\text{end}}$) would be to lower the bond strength estimates given above.

Mode-Specific, Nonadiabatic Dissociation Dynamics. The deduced energy disposal shows a number of interesting contrasts with that observed in the case of phenol following photoexcitation to low vibrational levels of its S(1$\pi\pi^*$) state. This first concerns the mechanism by which flux transfers to the $1\pi\sigma^*$ state, which, in the case of thiophenol, even at the longest excitation wavelengths, is deduced to involve (S–H torsion induced) coupling at the $1\pi\pi^*/1\pi\sigma^*$ CI. In contrast to the phenol case, there is no “shift” in the deduced $E_{\text{end}}$ of the peak at highest TKER upon varying $\lambda_{\text{phot}}$ implying a common fragmentation mechanism (i.e., via the $1\pi\pi^*/1\pi\sigma^*$ CI) across the wavelength range investigated. The evolving flux is therefore sensitive to the upper part of the CI between the diabatic $1\pi\sigma^*$ and $1\pi\pi^*$ PESs at longer R$_{S-H}$, in contrast to the case of phenol at long $\lambda_{\text{phot}}$, where the dissociating molecules are deduced to sample the lower part of the corresponding CI after internal conversion to high vibrational levels of the ground state. A second difference arises at the $1\pi\pi^*/1\pi\pi$ CI itself, where, in the case of the C$_6$H$_5$SH, dissociating flux has the opportunity to branch into two different electronic states of the C$_6$H$_5$S product. The corresponding first excited B$^2$ state in the phenoxyl radical lies $\sim 8900$ cm$^{-1}$ above the ground state, reflecting the much greater interaction between the singly occupied p$_z$ orbital of the heteroatom and the p system of the ring in the case of C$_6$H$_5$O. As a result, the $1\pi\pi^*/1\pi\pi$ CI in phenol occurs at shorter R$_{S-H}$ bond lengths, the difference in the respective potential gradients in the region of the intersection is much greater,
TABLE 2: Wavelengths and Wavenumbers of Prominent Peaks in the Action Spectrum for Forming D Atoms Following Photolysis of C₆H₅SD Molecules, Together with Vibronic Assignments Proposed by Analysis of the Accompanying TKER Spectra and the Approximate Vibrational Term Values (relative to the S₁ origin)

<table>
<thead>
<tr>
<th>λ_{photon} / nm</th>
<th>μ_{photon} / cm⁻¹</th>
<th>S₁ ← S₀ transition</th>
<th>S₁ term value / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>285.80</td>
<td>34990</td>
<td>0°</td>
<td>0</td>
</tr>
<tr>
<td>282.80</td>
<td>35360</td>
<td>6a₁</td>
<td>370</td>
</tr>
<tr>
<td>280.25</td>
<td>35680</td>
<td>12a₁</td>
<td>690</td>
</tr>
<tr>
<td>278.27</td>
<td>35940</td>
<td>10a₁</td>
<td>950</td>
</tr>
<tr>
<td>277.16</td>
<td>36080</td>
<td>15a₁</td>
<td>1090</td>
</tr>
<tr>
<td>275.31</td>
<td>36320</td>
<td>10a₁ + 6a₁</td>
<td>1330</td>
</tr>
<tr>
<td>274.42</td>
<td>36440</td>
<td>15a₁ + 6a₁</td>
<td>1450</td>
</tr>
</tbody>
</table>

Flux on the \( \nu^1 \) path shows a greater tendency to follow the diabatic pathway, and dissociation to electronically excited phenoxyl products is excluded on energetic grounds (except at much shorter \( \lambda_{photon} \), or following prior excitation to selected vibrational levels within the ground state.)

The product energy disposal can thus be rationalized as follows. Flux on the \( \nu^1 \) PES that follows the diabatic route through the \( \nu^1 \) CI evolves to H + C₆H₅S(\( \Sigma^2B_1 \)) products. Vibronic symmetry conservation requires that these products are formed in \( \nu^1 \) vibrational levels, as observed. Dissociation following excitation to the S₁ origin level results in population of product modes \( \nu_{16b} \) and \( \nu_{6a} \) as well as the \( \nu = 0 \) level. Activity in the former mode is understandable in terms of the (relatively weak, in-plane) impulse exerted by the departing H(D) atom, while the observed activity in \( \nu_{6a} \) likely reflects changes in this low-frequency ring vibration during the evolution from the excited parent molecule to product radical. Such excitations will be described as dynamic Franck-Condon (dFC) effects from hereon. As in phenol,³ activity in other \( \nu^1 \) vibrational modes (\( \nu_1, \nu_{6a}, \nu_{12}, \nu_{15}, \) and the \( \nu_{6a} + \nu_{12} \) combination mode in the case of thiophenol) identified when exciting at selected shorter wavelengths in this range can be explained in terms of conservation of “spectator” modes that are introduced in the S₁ \( \leftarrow \) S₀ excitation step and carry through, adiabatically, into the products. Such product excitations will henceforth be described as originating from vertical Franck-Condon (vFC) excitation within the parent. Given the close similarities in the wavenumbers of each of these conserved modes in the (ground-state) parent and the corresponding modes in both states of 2B₂ (see Appendix 1), identifying these modes offers a route to assigning the diffuse structure within the respective action spectra for forming H and D atoms. Assignments derived in this way for some of the more intense features in the action spectrum for forming D atoms from photolysis of C₆H₅SD (Figure 2c) are collected in Table 2. We note that the first three such separations match very well with those identified in the earlier analysis of the structured parent REMPI spectrum, implying that, at least with regards to these in-plane ring motions, the geometry of, and bonding within, the excited state providing the resonance enhancement is very similar to that in the \( \nu^1 \) (S₁) state.

Flux on the \( \nu^2 \) PES that follows the adiabatic route through the \( \nu^2 \) CI evolves to C₆H₅S(\( \Sigma^2B_1 \)) excited-state products. Vibronic symmetry conservation in this case requires that these products are formed in \( \nu^2 \) vibrational levels, again as observed. The most obvious features in this product channel when exciting via the S₁ origin indicate population of levels with \( \nu_{12} = 1 \) or \( \nu_{6a} = 1 \); no \( \nu = 0 \) products are observed. Interestingly, the recent PES studies of phenol dissociation via the corresponding \( \nu^1 \) CI identified activity in these same two coupling modes.³ As in that case, the implication of this vibrational assignment is that parent modes \( \nu_{12} \) and \( \nu_{6a} \) can both be activated by coupling at the \( \nu^1 \) CI, with the former seemingly the more active coupling mode in this case. These, and \( \nu_{15} \) will henceforth be referred to as CI-induced coupling modes. Population of other levels, involving \( \nu^1 \) modes in combination with \( \nu_{11} \) or \( \nu_{16a} \), is identifiable in spectra recorded at shorter \( \lambda_{photon} \). The active \( \nu^1 \) modes are largely the same as the dFC and vFC modes identified in the \( \Sigma^2B_1 \) radical products, but again, some subtle differences can be recognized. For example, the spectrum recorded at \( \lambda_{photon} = 290 \) nm reveals activity in \( \nu_{16b} \) (the in-plane C=S bend, which we have identified as a dFC mode) in the ground-state products but not in the \( \Sigma^2B_1 \) product channel. Is this simply a consequence of the reduced TKER associated with these excited state products (and thus the reduced impulse from the departing H/D atom), or does it hint that fragmentation to excited-state products is favored by nonplanar or more collinear dissociation geometries?

3.3.2. Photodissociation at Wavelegths \( \lambda_{photon} < 275 \) nm.

Product-Mode Assignments and Recoil Anisotropy. The Eᵣ(C₆H₅S) spectrum obtained following excitation of C₆H₅SH at \( \lambda_{photon} = 275.00 \) nm (Figure 5e) hides a subtlety; this is the longest-wavelength spectrum within which the faster features exhibit discernible recoil anisotropy. Recoil anisotropy can be seen more clearly in data recorded at shorter wavelengths, for both C₆H₅SH and C₆H₅SD. By way of illustration, Figure 8 shows Eᵣ(C₆H₅S) spectra from C₆H₅SH photolysis at \( \lambda_{photon} = 272.50 \) nm recorded with Eᵣ aligned at, respectively, \( \theta = 0 \) (c) and 90° (b) to the TOF axis. The structure evident in Figure 8b is reminiscent of that seen at the longest \( \lambda_{photon} \) (Figure 5a) and can be assigned accordingly, but these spectra also reveal more population of levels with higher internal energy, in both product channels. These data, together with the corresponding spectra recorded with Eᵣ aligned at \( \theta = 54.7° \), allow self-
normalization of the respective spectra and determination of the TKER (and \( E_{\text{int}}(\text{C}_6\text{H}_5\text{S}) \)) dependence of the recoil anisotropy parameter, \( \beta \) (Figure 8a).\(^{15} \) Three features of these data merit particular note. First, branching into the lowest energy levels of the excited \( \text{C}_6\text{H}_5\text{S}(^2\text{B}_2) \) products at \( \lambda_{\text{phot}} = 272.50 \) nm is noticeably stronger than that at \( \lambda_{\text{phot}} = 275.00 \) or 277.50 nm (Figure 5e and d). Second, the fastest features in both product channels are more prominent in the spectra recorded with \( \epsilon_{\text{phot}} \) perpendicular to the detection axis; the fastest features display a recoil anisotropy characterized by \( \beta \approx -0.45 \), whereas the unresolved signal appears essentially isotropic. The apparent \( \beta \) associated with the fastest \( \text{H} + \text{C}_6\text{H}_5\text{S}(^2\text{B}_2) \) products appearing at the same TKER \( \lambda_{\text{phot}} \). Third, the population distribution in both product channels spreads to higher \( \epsilon_{\text{int}}(\text{C}_6\text{H}_5\text{S}) \) as \( \lambda_{\text{phot}} \) is reduced, with the result that the “dip” separating the product channels in TKER spectra recorded at long \( \lambda_{\text{phot}} \) (see, e.g., Figure 5) gradually fills. The transition dipole moment for \( \text{S}_1 \leftarrow \text{S}_0(\pi^* \leftrightarrow \pi) \) excitation lies in the plane of the molecule and roughly parallel to the \( \text{S} \text{−} \text{H} \) bond, whereas the transition dipole associated with excitation to the \( ^1\pi\sigma^*(\text{S}_2) \) state lies normal to the plane of the benzene ring and thus also perpendicular to the \( \text{S} \text{−} \text{H} \) bond (at the planar equilibrium geometry). The isotropy of the recoiling products observed at \( \lambda_{\text{phot}} > 275 \) nm has been rationalized in terms of \( \text{S}_1 \leftarrow \text{S}_0 \) excitation, relatively slow transfer (by tunnelling) to the \( ^1\pi\sigma^*/1\pi\pi \) PES, and subsequent dissociation via the \( ^1\pi\pi^*/1\pi\pi \) CI at longer \( R_{\text{S}−\text{H}} \). Once \( \lambda_{\text{phot}} < 275 \) nm, the \( \text{C}_6\text{H}_5\text{S} \) fragments with the lowest internal energies in each product channel display perpendicular recoil anisotropy, whereas the more internally excited products continue to exhibit isotropic velocity distributions. Such behavior can be rationalized by assuming that excitation at \( \lambda_{\text{phot}} \approx 275 \) nm populates both the \( ^1\pi\pi^*(\text{S}_1) \) and \( ^1\pi\sigma^*(\text{S}_2) \) excited states directly. Extrapolating the trends observed at longer \( \lambda_{\text{phot}} \) suggests that vFC modes excited by \( \text{S}_1 \leftarrow \text{S}_0 \) excitation at these wavelengths will map into the corresponding vibrational motions in the \( \text{C}_6\text{H}_5\text{S} \) fragments.

Figure 9. Internal energy spectra of \( \text{C}_6\text{H}_5\text{S} \) radicals formed following excitation of \( \text{C}_6\text{H}_5\text{SH} \) at \( \lambda_{\text{phot}} = 275.50 \) nm, recorded with \( \epsilon_{\text{phot}} \) aligned at \( \theta = 90^\circ \) (b) and \( 0^\circ \) (c) to the TOF axis; (a) shows the deduced variation of \( \beta \) with \( E_{\text{int}}(\text{C}_6\text{H}_5\text{S}) \) and thus TKER.

Excitation in spectator modes will provide negligible enhancement to the \( ^1\pi\pi^*(\text{S}_1) \) to \( ^1\pi\sigma^* \) tunnelling probability, and given the time scales involved, the internally excited products that result would be expected to show little recoil anisotropy, as observed. The \( \text{S}_1 \leftarrow \text{S}_0(\sigma^* \leftarrow \pi) \) excitation, in contrast, populates an excited state that dissociates directly. Symmetry requires that the resulting products should show perpendicular recoil anisotropy (i.e., \( \beta \approx 0 \)), again as observed. The vibrational energy disposal accompanying direct dissociation on the \( ^1\pi\pi^* \) PES is found to mimic that observed at \( \lambda_{\text{phot}} \approx 290 \) nm, where the same \( ^1\pi\sigma^* \) PES is deduced to be accessed by tunneling of \( \text{S}_1 \) molecules prepared with no internal excitation, supporting the view that this product branching is determined largely by the \( ^1\pi\pi^*/1\pi\pi \) CI.

Many of the trends noted when comparing the \( \lambda_{\text{phot}} = 272.50 \) nm data with that obtained at longer wavelength become increasingly evident as \( \lambda_{\text{phot}} \) is reduced further. As Figure 9 shows, the fastest features in both product channels formed at \( \lambda_{\text{phot}} = 275.50 \) nm exhibit perpendicular anisotropy (\( \beta \approx -0.85 \) for the fastest \( \text{H} + \text{C}_6\text{H}_5\text{S}(^2\text{B}_2) \) products), whereas again, the unresolved signal appears more isotropic. A similar preference for perpendicular recoil was also identified in the recent ion imaging studies of \( \text{H} \text{(D)} \) atom photoproducts from \( \text{C}_6\text{H}_5\text{SH(}C_6\text{H}_5\text{SD}) \) photolysis at \( \lambda_{\text{phot}} = 243.1 \) nm.\(^{10,11} \) Figure 10 shows TKER spectra obtained when exciting with \( \epsilon_{\text{phot}} \) aligned perpendicular to the TOF axis at several well-separated wavelengths in the range of \( 230.0 \leq \lambda_{\text{phot}} \leq 260.0 \) nm. Short
progressions attributable to formation of C₆H₅S(X²B₁) products with ν₁≤3 are evident in all but the λₚhot = 230.0 nm spectrum, as is a peak associated with C₆H₅S(2B₂), ν₁ = 1) fragments. The excited-state product channel is particularly evident in the λₚhot = 245 nm spectrum (i.e., at photolysis wavelengths close to that investigated by Lim et al.¹⁰,¹¹), and additional structure attributable to the population of levels involving activity in ν₁5 as well as ν₁ is apparent. The family of spectra shown in Figure 10 provides further illustration of the progressive coalescence of the TKER distributions associated with the C₆H₅S(X²B₁) and C₆H₅S(2B₂) product channels and of the substantial contribution from the broad feature centered at low TKER that we attribute to “statistical” decay of highly internally excited parent molecules (recall Figure 4c), both of which lead to a progressive loss of structure in TKER spectra recorded at shorter λₚhot.

Recalling the parent absorption spectrum (Figure 1) and the calculated vertical excitation energies (Table 1), it is evident that the dominant excitation at λₚhot ≤ 260 nm is likely to be to the S₁(1ππ*)(b) state. The present TD-DFT calculations show the S₁ ← S₀ transition moment lying in the plane of the molecule but at ~90° to the S–H bond. Discussion of the fragmentation mechanism at these shorter wavelengths must, of necessity, be speculative, given our ignorance of the one or more CIIs that facilitate population transfer from the photoprepared S₁ state to, for example, the dissociative 1πσ* PES. The observed recoil anisotropy of the fastest C₆H₅S(X²B₁) and C₆H₅S(2B₂) products indicates that such transfer must be fast and efficient, but the increased yield of slow H atoms in the measured spectra (Figures 4c and 10) points to alternative fragmentation channels also.

Photolysis of C₆H₅SD and the Origin of the Slow H Atom Signal. Analysis of TKER spectra derived from D atom TOF measurements following photolysis of C₆H₅SD in this same wavelength range provides some insights into these alternative fragmentation processes. The spectrum obtained by monitoring D atoms following excitation at λₚhot = 250.0 nm (Figure 11a) shows two maxima, attributable to S–D bond fission on the 1πσ* PES and formation of C₆H₅S products in their X²B₁ and 2B₂ electronic states (as found when monitoring H atom products from C₆H₅SH at similar wavelengths), but the relative yield of slow products is greatly reduced. To assess the extent of deuteration in the C₆H₅SD sample, TOF spectra were also recorded at λₚhot = 243.136 and 243.069 nm, wavelengths appropriate for two-photon 2s ← 1s excitation of, respectively, any H and D atom products, without the presence of the Lyman-α probe laser pulse (or the 364.7 nm radiation from which it is derived). Any H⁺/D⁺ ions formed by 2 + 1 REMPI at the λₚhot wavelength were promptly extracted by the 25 V cm⁻¹ field that spans the interaction volume, but neutral H/D (n = 2) atoms that avoided ionization were then excited with the ~366 nm Rydberg tagging laser pulse and their TOFs detected in the usual manner. The TKER spectrum obtained at λₚhot = 243.069 nm (Figure 11b, resonant with the 2s ← 1s transition of D) is similar to that obtained at λₚhot = 250.0 nm and can be interpreted accordingly. The spectrum obtained at λₚhot = 243.136 nm (Figure 11c, resonant with the 2s ← 1s transition of H) shows some signal at TKER ~ 12750 and ~10000 cm⁻¹, attributable to formation of H + C₆H₅S(X²B₁) and H + C₆H₅S(2B₂) products, implying the presence of some residual C₆H₅SH in the C₆H₅SD sample. More revealing, however, is the dominant feature at low TKER, which is barely evident in the corresponding spectrum obtained by monitoring D atom products (Figure 11b). The ratio of “fast” to “slow” H atoms in this spectrum is much smaller than that in the corresponding spectrum from C₆H₅SH (recall Figure 4c), confirming that most of this slow H atom signal must arise from C₆H₅SD dissociation. As commented previously, these slow products are most readily attributable to unimolecular decay of highly vibrationally excited parent molecules in their ground electronic state (formed by radiationless transfer following one- or multi-photon excitation). The preponderance of H rather than D atom products at low TKER hints at the operation of competing C–H bond fission processes in the statistical decay of such highly excited parents, but any fuller discussion of such decays must await more detailed knowledge of the ground-state PES, the molecular rearrangements that it can support prior to fragmentation, and the possible kinetic isotope effects that might discriminate against D atom loss.

4. Conclusions

This translational spectroscopy study of the H(D) atom photofragments from C₆H₅SH(C₆H₅SD) confirms S–H(S–D) bond fission as a primary dissociation process throughout the 225 ≤ λₚhot ≤ 290 nm wavelength range investigated. The partner C₆H₅S fragments are formed in both their ground (X²B₁) and first excited (2B₂) electronic states, in a spread of vibrational levels that broadens and shifts to higher E_v(d(C₆H₅S)) as λₚhot is reduced. Analysis of parent excitation spectra, of resolvable vibrational structure within the TKER spectra of the H(D) + C₆H₅S products, and of the recoil anisotropy of these fragments leads to the following conclusions. Excitation at λₚhot > 275 nm results in population of quasi-bound levels of the 1ππ*(S₁) state, which decay by tunneling to the 1πσ* PES. Torsional motion of the S–H group is identified as a likely coupling mode, facilitating population transfer at the CI between the diabatic 1ππ* and 1πσ* PESs. Flux evolving on the 1πσ* PES samples a second CI, at longer R_s–H, between the diabatic 1πσ* and 1ππ PESs, where the branching between ground-...
state \( \text{C}_6\text{H}_5\text{S} \) fragment formation is established. The populated vibrational levels in each product channel have to satisfy symmetry conservation. All populated levels of \( \text{C}_6\text{H}_5\text{S}(X^2\text{B}_1) \) identified in the TKER spectra have a \(^1\) vibrational symmetry; the in-plane modes identified as active can be understood in terms of vertical (and/or dynamic) Franck–Condon effects. The vibrational energy disposal within the \( \text{C}_6\text{H}_5\text{S}(X^2\text{B}_2) \) products is very different, involving levels with \(^v\) vibrational symmetry, particularly modes \( \nu_{11} \) and \( \nu_{16a} \). As in phenol, the corresponding parent modes are deduced to promote coupling to the \(^1\pi\sigma^* / 1\pi\pi^* \) \( \text{C}_6\text{H}_5\text{O} \). Such detailed vibrational assignments allow new and improved determinations of the bond dissociation energies, \( D_0(\text{C}_6\text{H}_5\text{S} \rightleftharpoons \text{H}) = 28030 \pm 100 \text{ cm}^{-1} \) and \( D_0(\text{C}_6\text{H}_5\text{S} \rightleftharpoons \text{D}) = 28610 \pm 100 \text{ cm}^{-1} \), and of the energy separation between the \( X^2\text{B}_1 \) and \( 2\text{B}_2 \) states of the \( \text{C}_6\text{H}_5\text{S} \) radical, \( T_{\text{hom}} = 2800 \pm 40 \text{ cm}^{-1} \).

Details of the energy disposal evolve as \( \lambda_{\text{phot}} \) is reduced. Once \( \lambda_{\text{phot}} \leq 275 \text{ nm} \), the fastest \( \text{C}_6\text{H}_5\text{S} \) fragments in both product channels display anisotropic recoil velocity distributions, with a preference for \( \mathbf{v} \) being perpendicular to \( \mathbf{e}_{\text{phot}} \) and thus to the transition dipole moment. This finding is interpreted in terms of direct \( S_1 \rightleftharpoons S_0(\sigma^* \rightleftharpoons \pi) \) excitation and prompt dissociation on the \(^1\pi\sigma^*/1\pi\pi^* \) PES, with subsequent product branching determined by the \(^1\pi\sigma^*/1\pi\pi^* \) CI, as seen at longer \( \lambda_{\text{phot}} \). \( S_1 \rightleftharpoons S_0(\sigma^* \rightleftharpoons \pi) \) excitation is also deduced to occur at these same wavelength.

Franck–Condon considerations require that the resulting \( S_1 \) parent molecules are necessarily vibrationally excited but predominantly in “spectator” modes that are, at best, weakly coupled to the dissociation coordinate. Such molecules are deduced to dissociate by tunneling to the \(^1\pi\sigma^* \) PES in much the same way as that at longer \( \lambda_{\text{phot}} \), with excitation in the “spectator” modes mapping through into the corresponding product vibrational levels. Not all of the excess energy is thus available for release as kinetic energy, and the formation of such products leads to a progressive broadening and loss of structure in TKER spectra measured at shorter \( \lambda_{\text{phot}} \). Once \( \lambda_{\text{phot}} \leq 260 \text{ nm} \), \( S_1 \rightleftharpoons S_0(\pi\pi^* \rightleftharpoons \pi\pi^*) \) excitation dominates, but the observed energy disposal and the evident recoil anisotropy of the fastest \( \text{C}_6\text{H}_5\text{S}(X^2\text{B}_1) \) and \( \text{C}_6\text{H}_5\text{S}(2\text{B}_2) \) products indicates that coupling between the \( S_1 \) and \(^1\pi\sigma^* \) states via one or more, as yet unknown, CIs must be both fast and efficient. The relative increase in the yield of slow H atoms following excitation at short \( \lambda_{\text{phot}} \) suggests that other fragmentation channels, most probably involving unimolecular decay of highly vibrationally excited ground-state molecules, also gain in importance.

The UV photochemistry of gas-phase thiophenol shows similarities with, but also a number of significant differences from, that of the first-row analogue, phenol. Both molecules dissociate by \( \text{X} \rightleftharpoons \text{H} \) bond fission following excitation at the respective \( S_1 \rightleftharpoons S_0 \) origins and at all shorter \( \lambda_{\text{phot}} \). In both cases, the decay rate from low levels of the respective \( S_1 \) states is sufficiently slow that the resulting H atoms show isotropic recoil velocity distributions. However, the lack of \( 1 + 1 \) REMPI signal via the \( S_1 \) state of thiophenol and the widths of individual features in the action spectra for forming H(D) atoms following \( S_1 \rightleftharpoons S_0 \) excitation of \( \text{C}_6\text{H}_5\text{SH}(\text{C}_6\text{H}_5\text{SD}) \) both indicate that the lifetime of thiophenol(\( S_1 \)) molecules is much shorter than that of phenol(\( S_1 \)) molecules at comparable levels of excitation. The reduced lifetime of thiophenol(\( S_1 \)) molecules can be traced to improved coupling to the dissociative \(^1\pi\sigma^* \) state, the energy of which is lower in thiophenol (relative to that of the valence \(^1\pi\pi^* (\text{S}_1) \) state) than in phenol, mirroring the differences in parent ionization potential \( [8.30 \text{ eV (thiophenol)}, 18.85 \text{ eV (phenol)}]^{33} \). Photoincited \( \text{C}_6\text{H}_5\text{SH} \) molecules are thus deduced to dissociate either by (torsionally mediated) tunneling to the \(^1\pi\sigma^*/1\pi\pi^* \) PES via the \(^1\pi\pi^*/1\pi\sigma^* \) CI and/or, once \( \lambda_{\text{phot}} \leq 275 \text{ nm} \), following direct population of this \( S_2(^1\pi\pi^*) \) state. In either scenario, the dissociating flux samples the upper part of the subsequent \(^1\pi\sigma^*/1\pi\pi^* \) CI at longer \( r_{\text{SH}} \), where the branching into specific vibrational levels of the ground \( (X^2\text{B}_1) \) and first excited \( (2\text{B}_2) \) states of the \( \text{C}_6\text{H}_5\text{S} \) fragment is determined.

Phenol(\( S_1 \)) molecules, in contrast, are deduced to dissociate by internal conversion to vibrational levels of the ground state. Subsequent \( \text{O} \rightleftharpoons \text{H} \) stretching motion on the \(^1\pi\pi^*/1\pi\sigma^* \) CI and/or the much greater energy separation between the \( X^2\text{B}_1 \) and \( 2\text{B}_2 \) states in \( \text{C}_6\text{H}_5\text{O} \), apparently precludes formation of excited-state \( \text{C}_6\text{H}_5\text{O} \) radicals in \( \text{C}_6\text{H}_5\text{OH} \) photolysis at all UV wavelengths studied thus far.

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Appendix 1

In the following table, B3LYP harmonic wavenumbers for the fundamental vibrational modes of \( \text{C}_6\text{H}_5\text{SH} \) in its ground state and for the \( \text{C}_6\text{H}_5\text{S} \) radical in its ground \( (X^2\text{B}_1) \) and first excited \( (2\text{B}_2) \) electronic states, numbered as in phenol (ref. S) using the Wilson mode labelling scheme and ordered on the basis of the \( \text{C}_{2v} \) symmetry labels of the radical products, are given. Anharmonic wavenumbers for these fundamental modes of vibration are listed for the respective ground states also.

References and Notes


