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Near Ultraviolet Photolysis of 2-thiophenethiol†

Rebecca A. Ingle, a Tolga N. V. Karsili, a Gregg Dennis, a Michael Staniforth, b Vasilio G. Stavros, b and Michael N. R. Ashfold a

H atom loss following near ultraviolet photoexcitation of gas phase 2-thiophenethiol molecules has been studied experimentally, by photofragment translational spectroscopy (PTS) methods, and computationally, by ab initio electronic structure calculations. The long wavelength (277.5 ≥ λ_{shot} ≥ 240 nm) PTS data are consistent with S–H bond fission after population of the first $^1\pi\sigma^*$ state. The partner thiophenethyl (R) radicals are formed predominantly in their first excited $^2\Delta'$ state, but assignment of a weak signal attributable to H + R($^2\Sigma'$) products allows determination of the S–H bond strength, $D_0 = 27800 \pm 100$ cm$^{-1}$ and the $^2\Delta'$–$^2\Sigma'$ state splitting in the thiophenethyl radical ($\Delta E = 3580 \pm 100$ cm$^{-1}$). The deduced population inversion between the $^2\Delta'$ and $^2\Sigma'$ states of the radical reflects the non-planar ground state geometry (wherein the S–H bond is directed near orthogonal to the ring plane) which, post-photoexcitation, is unable to planarise sufficiently prior to bond fission. This dictates that the dissociating molecules follow the adiabatic fragmentation pathway to electronically excited radical products. $^2\pi ← ^2\pi$ absorption dominates at shorter excitation wavelengths. Coupling to the same $^1\pi\sigma^*$ PES remains the dominant dissociation route, but a minor yield of H atoms attributable to a rival fragmentation pathway is identified. These products are deduced to arise via unimolecular decay following internal conversion to the ground ($^3\Sigma_0^+$) state potential energy surface via a conical intersection accessed by intra-ring C–S bond extension. The measured translational energy disposal shows a more striking change once $\lambda_{shot} ≤ 220$ nm. Once again, however, the dominant decay pathway is deduced to be S–H bond fission following coupling to the $^1\pi\sigma^*$ PES but, in this case, many of the evolving molecules are deduced to have sufficiently near-planar geometries to allow passage through the conical intersection at extended S–H bond lengths and dissociation to ground ($\bar{X}$) state radical products. The present data provide no definitive evidence that ring opening can compete with fast S–H bond fission following near UV photoexcitation of 2-thiophenethiol.

1 Introduction

Many recent studies have illustrated the importance of X–Y (X = O, S, etc, Y = H, CH$_3$, etc) bond fission following near UV excitation of (thio)phenols$^{1–17}$ and (thio)anisoles,$^{18–29}$ in the gas phase. The translational energy distributions of the resulting photofragments generally peak at energies well above zero, consistent with dissociation on an excited state potential energy surface (PES) that is repulsive with respect to X–Y bond extension. Such excited states are formed by electron promotion from one of the highest occupied molecular orbitals (typically a non-bonding (n) orbital centred on the heteroatom or a delocalised $\pi$ bonding orbital) to an anti-bonding $\sigma^*$ orbital centred around the X–Y bond. For compactness, these states are henceforth simply termed $\pi\sigma^*$ excited states and the narrative will focus solely on singlet states of the molecule.

In many cases, the first $\pi\sigma^*$ PES in these molecules shows a shallow minimum in the Franck-Condon region, due to Rydberg/valence mixing.$^{19,30}$ In the planar limit, the ground ($S_0$) state correlates diabatically with a Y atom/radical together with the X-containing radical (henceforth R) in its first excited ($\bar{A}$) electronic state upon X–Y bond extension, while the $\pi\sigma^*$ PES correlates with the ground ($\bar{X}$) state of the radical. In a simple orbital picture, the $\bar{X}$ and $\bar{A}$ states of R are distinguished by whether the odd electron is in, respectively, a $p_x$ or $p_y$ orbital of the heteroatom, and their relative energies reflect the conjugation (or not) of this odd electron with the $\pi$ system of the ring. The
\[ \pi^+ \leftarrow \pi \] absorption profiles in molecules of this type typically lie at similar energies to the \( \pi^+ \leftarrow \pi \) excitations discussed above, and typically have larger cross-sections. Thus the relative probability of exciting a \( \pi^+ \leftarrow \pi \) or \( \sigma^+ \leftarrow \pi \) transition is likely to be wavelength dependent. In a diabatic picture, the \( \pi^+ \) excited state is bound with respect to extending \( R_{X-Y} \). Nonetheless, molecules excited to the \( \pi^+ \) state typically still undergo \( X-Y \) bond fission, by radiationless transfer mediated by a CI between the \( \pi^+ \) and \( \pi\sigma^+ \) PESs at shorter \( R_{X-Y} \). Henceforth, we will use the labels CI-1 and CI-2 to distinguish the \( \pi^+ / \pi\sigma^+ \) and \( \pi\sigma^+ / S_0 \) CIs.

The present study focuses on the near UV photochemistry of 2-thiophenethiol (fig. 1), which offers a test-bed for exploring photoinduced fission of an \( S-H \) bond attached to an aromatic ring using a combination of photofragment translational spectroscopy (PTS) and \textit{ab initio} electronic structure methods. It also offers an opportunity to revisit conclusions reached in an earlier study of the photodissociation dynamics of a related heterocycle, 2-methyl-3-furanthiol. S-H bond fission on the \( \pi\sigma^+ \) PES is shown to be a major H atom formation channel at all wavelengths studied, but we appreciate that other fragmentation pathways may also be active. For example, an early PTS study following 193 nm excitation of thiophenol found evidence of a competing C-S bond cleavage pathway, yielding \( C_5H_4 + SH \) products, although the present study is blind to any such products.

2 Methodology

2.1 Experimental

The H Rydberg atom (HRA)-PTS experiment has been described previously, so only a summary and details of some recent experimental upgrades, will be given here. 2-thiophenethiol (\( \geq 90 \% \) purity, Sigma Aldrich) was used without further purification. The sample was heated to \( \approx 50 \)°C and the resulting vapour then supersonically expanded in \( \approx 400 \) mbar of argon seed gas (BOC Gases, CP grade) to form the pulsed molecular beam (10 Hz). The molecular beam was intersected with a tuneable UV photolysis pulse generated by frequency-doubling the output of a Nd:YAG pumped dye laser (208 nm \( \leq \lambda_{\text{phot}} \leq 277.5 \) nm). 277.5 nm was the longest photolysis wavelength at which measurable H atom signal was detected. H atom photoproducts formed in the interaction region were then excited to high-lying (\( n \approx 80 \)) Rydberg states using a double-resonant process involving 121.6 nm (Lyman-\( \alpha \)) and 366 nm laser pulses both delayed with respect to the photolysis pulse by \( \delta t \approx 10 \) ns. H atom photoproducts formed with recoil velocities aligned with the detection axis travel through a field- and collision-free time-of-flight region prior to passing through a grounded mesh positioned \( \approx 1 \) cm in front of a new microchannel plate (MCP) detector. The total flight length (\( d \)) from the interaction region with the new detector arrangement is 0.605 m. Product recoil anisotropy parameters (\( \beta \)) were estimated by comparing time-of-flight (TOF) spectra recorded with the polarisation vector of the photolysis laser, \( \varepsilon_{\text{phot}} \), aligned at \( \theta = 0^\circ, 54.7^\circ \) and \( 90^\circ \) to the TOF axis.

The apparatus and procedures for the time-resolved velocity map ion imaging (TR-VMI) experiments have also been detailed elsewhere, and the 2-thiophenethiol sample was introduced into the spectrometer using an Even-Lavie pulsed solenoid valve operating at a 125 Hz repetition rate with a typical opening time of 14 \( \mu s \), seeded in 2 bar of He. The 800 nm output of a Ti:Sapphire oscillator and regenerative amplifier system was used to pump two optical parametric amplifiers to generate UV pump (235 nm \( \leq \lambda_{\text{phot}} \leq 260 \) nm) and probe (243.1 nm) pulses. We also extended the wavelength of our probe to 200 nm (\( \approx 1 \) \( \mu J/pulse \)), by performing frequency mixing in a series of type-I and type-II \( \beta \)-barium borate crystals. The temporal delay between the pump and probe pulses was user variable out to \( \delta t \approx 1.2 \) ns. H atom photofragments formed in the interaction region were ionised by the probe pulse via (2 + 1) resonance-enhanced multiphoton ionisation at 243.1 nm. Velocity map images of \( H^+ \) ions...
were recorded using a pair of MCPs coupled to a P-43 phosphor screen with a CCD camera and the 3-D distributions reconstructed from the crushed ion images using the polar onion-peeling (POP) algorithm. The instrument response function (IRF) was characterised by the non-resonant multiphoton ionisation of methanol, yielding an IRF of \( \approx 120 \text{ fs at } \lambda_{\text{phot}} \geq 238 \text{ nm or } \approx 150 \text{ fs at } 200 \text{ nm.} \)

2.2 Theoretical

The ground state geometry of 2-thiophenethiol was optimised using MP2/aug(S)-AVTZ, where AVTZ = aug-cc-pVTZ augmentation of the basis set and SA-CASSCF showed that (i) augmentation of the basis set by single point energy corrections carried out using the larger 6-311+G(d,p) basis set. Potential transition states between transition state and parent ions on the S0 PES were optimised using the Synchronous Transit-Guided Quasi-Newton Method using the DFT/B3LYP/6-31G(d) level of theory and the various isomers as structural guesses. Anharmonic normal mode vibrational wavenumbers for the ground state R radical were calculated using DFT/B3LYP/6-31G(d,p).

The MP2/aug(S)-AVTZ, CCSD(T)(F12) and CASSCF/CASPT2 calculations were calculated in Gaussian 09. The MP2/cc-pVDZ and DFT calculations in Gaussian 09 and the ADC(2) calculations in Turbomole.

3 Results and Discussion

3.1 Parent Molecule Spectroscopy

Fig. 2 shows the UV absorption spectrum of a room temperature gas phase sample of 2-thiophenethiol over the range 200 \( \leq \lambda_{\text{phot}} \leq 310 \text{ nm.} \) This absorption profile can be rationalised by reference to Table 1, which lists the vertical excitation energies and oscillator strengths calculated using CASPT2 and CASSCF, and the various potential energy cuts (PECs) presented later in the paper. The broad, intense feature that plateaus at \( \approx 230 \text{ nm} \) is most plausibly attributed to the second ring-centred \( \pi^* \leftarrow \pi \) transition, with the predicted \( 1^1\pi\pi^* \leftarrow S_0 \) and \( 1^1\sigma^* \leftarrow S_0 \) excitations contributing to a weaker tail extending to longer wavelengths.

![Absorbance vs Wavelength](image_url)

Fig. 2 UV absorption spectrum of room temperature, gas phase 2-thiophenethiol recorded over the wavelength range 200 \( \leq \lambda_{\text{phot}} \leq 310 \text{ nm.} \)
bond directed at $\psi = 80^\circ$ to the ring plane. This can be understood by recognising that the S1 atom is $sp^2$ hybridised and thus has a partial positive charge as its lone pair is delocalised around the ring. This renders the 2- and 3- positions nucleophilic. As SH is a weak $\pi$ donor, planar ($\psi = 0^\circ$ or $180^\circ$) configurations would involve unfavourable electrostatic interactions between the $3p_x$ orbital on S6 and the ring $\pi$ system. A $\psi = 80^\circ$ configuration both precludes this destabilising interaction and allows the $\sigma^*$ orbital around the S6–H bond to accept the electron density at the 2– position. Fig. 3 suggests that the torsional barrier in the ground state is $\approx 600 - 700$ cm$^{-1}$.

### 3.2 HRA-PTS studies

Fig. 4 shows the total kinetic energy release (TKER) spectra derived from H atom TOF spectra measured at several different photolysis wavelengths in the range $239 \leq \lambda_{\text{phot}} \leq 277.5$ nm. TKER distributions were derived using Equation 2.

$$\text{TKER} = \frac{1}{2}m_H \left(\frac{d}{t}\right)^2 \left(1 + \frac{m_H}{m_R}\right)$$

(2)

where $m_H$ is the mass of the H atom (1.0079 au) and $m_R$ is the mass of the radical co-fragment formed on photodissociation, which we assume to have the chemical formula C$_3$H$_7$S$_2$ (115.20 u), $d = 0.6045$ m and $t$ is the H atom TOF. A $t^{-3}$ Jacobian was used when re-binning the measured intensities from TOF to TKER space and, as usual, we choose to report the TKER in cm$^{-1}$.

Each spectrum shows a relatively clear onset at high TKER but also extends to near zero kinetic energies, implying that some of the co-fragments are formed highly internally excited. The TKER associated with the high energy ‘peak’ in each spectrum, starred in fig. 4, increases linearly with increasing photolysis energy. We start by associating this peak with formation of co-fragments in their zero-point ($v=0$) vibrational level. Energy conservation arguments then allow us to estimate an S–H bond dissociation energy $D_0(R–H) \approx 31550$ cm$^{-1}$. This implied bond strength is significantly higher than that determined for bare and several substituted thiophenols, but similar to previously determined threshold energies for forming electronically excited (i.e. $\tilde{A}$ state) thiophenoxyl radicals. This encouraged more careful scrutiny of the measured TKER spectra, several of which do show a weak pedestal at TKERs extended beyond the starred feature. The bottom panel in fig. 4, which shows an expanded view of this high energy region in the 239 nm data, reveals a weak step comprising a fast peak at TKER $\approx 13950$ cm$^{-1}$ and extending to lower TKER. The energy spacing between this feature and the starred feature in fig. 4(e) is 3580 $\pm$ 100 cm$^{-1}$. Associating this faster onset with the formation of H + R($\tilde{X}$, $v=0$) fragments returns a bond dissociation energy $D_0(R–H) = 27800 \pm 100$ cm$^{-1}$ that is sensibly consistent with documented S–H bond strengths in other aromatic thiols.

This analysis implies a near total population inversion between the $\tilde{A}^2A'$ and $\tilde{X}^2A''$ electronic states of the radical co-fragment. Such dramatic branching between the electronic states of a photoproduct is not without precedent: the thiophenoxyl products formed by UV photolysis of thioanisole and various substituted thioanisoles are mostly formed in their excited ($\tilde{A}$) electronic state. This has been explained by considering the forces acting...
on the thioanisole molecules as they evolve on the $\pi\sigma^*$ PES. The $\pi\sigma^*$ PES in this case is accessed by radiationless transfer following photoexcitation to the $1\pi\pi^*$ state. This transfer is facilitated by out-of-plane distortions that persist as $R_{S-H}$ extends towards values associated with CI-2. Being non-planar in this region ensures that the molecules follow the adiabatic dissociation path, and electronically excited thiophenoxyl radical products are the inevitable result.

Most of the spectra in fig. 4 show one or more peaks at TKER values just below TKER$_{\text{max}}$. These are most plausibly attributed to population of specific vibrational levels of the $R(\bar{A})$ co-fragment. The more prominent intervals observed in two or more spectra lie $\approx 470$, $\approx 1000$ and $\approx 1450$ cm$^{-1}$ below the TKER$_{\text{max}}$ peak. Comparing these intervals with calculated anharmonic wavenumbers for the various vibrational fundamentals of the $R(\bar{X})$ radical - listed in the ESI - suggests preferential population of levels carrying one quantum of $v_{14}$, $v_{10}$ and $v_{14}$. All three are in-plane ring-breathing modes, population of which can most readily be understood on Franck-Condon grounds given the change in the ring $\pi$-bonding during the initial parent photo-excitation step and in the subsequent evolution to $R(\bar{A})$ fragments.

Angular anisotropy measurements at $\lambda_{\text{phot}} = 270$ and 240 nm both showed a higher relative yield of faster H atoms (e.g. products with TKER $>3000$ cm$^{-1}$) when $\varepsilon_{\text{phot}}$ was aligned perpendicular to the TOF axis (i.e. at $\theta = 90^\circ$). Here, we estimate a $\beta$ value of about $-0.5$. Recalling fig. 2, it is likely that the dominant excitation changes from some mix of $\sigma \leftarrow \pi$ and $\pi^* \leftarrow \pi$ excitations (at 270 nm) to predominantly $2\,^1\pi\pi^* \leftarrow S_0$ across this wavelength range but, as Table 1 shows, all three transition dipole moments are calculated to lie predominantly in the ring plane, and thus near perpendicular to the $S6-H$ bond. The observed recoil anisotropy follows naturally in the limit of prompt dissociation and near axial H atom recoil.

The foregoing discussion also accords with the observed electronic branching in the $R$ products. Fig. 5 shows two sets of PECs for the ground and first few excited singlet states of 2-thiophenethiol along $R_{S-H}$. The solid curves are calculated with $\psi = 80^\circ$ (the ground state equilibrium geometry), while those shown by dashed lines are for $\psi = 0^\circ$. In both cases, $\psi$ is clamped and the $S6-H$ bond incremented with the remainder of the nuclear framework held fixed at the ground state equilibrium geometry. Fig. 5 reiterates the similar vertical excitation energies of the $S_1$ and $S_2$ states (recall Table 1) and illustrates the expected CI between the $1\pi\sigma^*$ and $S_0$ PECs at $R_{S-H} \approx 2.6$ Å and $\psi = 0^\circ$ (the analogue of CI-2 in the thiophenols). It also highlights the preferred planar geometry of molecules in the $1\pi\sigma^*$ excited state. The observed product branching and recoil anisotropy both imply that, following UV photoexcitation, $R_{S-H}$ in the dissociating molecules must extend beyond that required for radiationless transfer through CI-2, i.e. before the $S6-H$ bond rotates into the ring plane. As such, the photoexcited molecules follow the adiabatic path towards dissociation to yield $H + R(\bar{A})$ products.

TKER spectra derived from H atom TOF spectra measured at several shorter wavelengths in the range 208.5 $\leq \lambda_{\text{phot}} \leq 230$ nm are shown in fig. 6. The 230 and 225 nm data are sensibly consistent with that obtained at longer photolysis wavelengths, with an obvious fast peak (starred) that we associate with formation of $R(\bar{A}, v=0)$ products. The TKER spectrum obtained at 220 nm (fig. 6(c)) shows several noteworthy differences. The $H + R(\bar{A}, v=0)$ peak is no longer evident (its expected position is indicated by the star), and the relative yield of slower products is increased. Of greater significance, however, the TKER spectrum shows clear signal out to that associated with formation of $H + R(\bar{X}, v=0)$ products. Measurements with $\varepsilon_{\text{phot}}$ aligned at $\theta = 0^\circ$, $54.7^\circ$ and $90^\circ$ suggest that these fast products have negligible recoil anisotropy ($\beta \approx 0$). The data obtained at 208 nm data shows some similarities – the relative yield of slow products is clearly increased, and an isotropic signal is still evident at TKERs greater than that expected for $H + R(\bar{A}, v=0)$ products – but also some differences – most notably the minimum at TKER $\approx 7000$ cm$^{-1}$. We chose to consider the additional insights provided by the TR-VMI studies before presenting a plausible rationale for the $\lambda_{\text{phot}}$ dependence of these TKER spectra.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Unrelaxed PECs along $R_{S-H}$ calculated at the CASPT2(10,8)/cc-pVDZ level for the ground and first three singlet excited states for 2-thiophenethiol with $\psi = 80^\circ$ (filled points and solid lines) and $\psi = 0^\circ$ (open points and dashed lines).}
\end{figure}

3.3 Time-Resolved Velocity Map Imaging

Fig.7 shows images of the H atom fragments (monitored via the $H^+$ ion) resulting from photolysis of 2-thiophenethiol at (a) 260, (b) 238 and (c) 200 nm, measured at $\delta t = 500$ fs. The left half of each image shows the recorded $H^+$ ion image, the right half shows a slice through the centre of the reconstructed 3-D ion distribution, and the white arrow indicates the alignment of $\varepsilon_{\text{phot}}$. The TKER spectra derived from these images, and from corresponding images measured at a longer pump-probe time delay ($\delta t = 50$ ps) are shown alongside. Again, we have assumed that the co-fragments partnering the observed H atoms have $m_H$ = 115.20 u. Though of lower energy resolution, the overall appear-
Table 1 Calculated vertical excitation energies, oscillator strengths (f) and transition dipole moments for the first four excited singlet states of 2-thiophenethiol, calculated at the CASSCF(10/10)/cc-pVDZ level of theory. Vertical excitation energies were energy corrected using CASPT2(10/10)/cc-pVDZ.

| Transition  | Energy / eV | f     | \(\mu_x\) | \(\mu_y\) | \(\mu_z\) | Transition Character |
|-------------|-------------|-------|------------|------------|------------|---------------------|
| \(S_1\rightarrow S_1\) | 5.49        | 0.024 | 0.013      | -0.395     | -0.081     | \(\pi\pi^*\)        |
| \(S_2\rightarrow S_1\) | 5.51        | 0.004 | -0.002     | 0.033      | 0.165      | \(\pi\sigma^*\) (S-H) |
| \(S_1\rightarrow S_0\) | 5.55        | 0.365 | 0.185      | -0.115     | 1.399      | \(\pi\pi^*\)        |
| \(S_2\rightarrow S_0\) | 6.49        | 0.001 | 0.081      | -0.010     | 0.007      | \(\pi\sigma^*\) (C-S) |

Fig. 6 TKER spectra derived from H atom TOF spectra measured following the photodissociation of 2-thiophenethiol at \(\lambda_{phot}\) = a) 230 nm, b) 225, c) 220 nm and d) 208.5 nm. The star shows the TKER expected for H + R(\(\tilde{\chi}\), \(v=0\)) products at each excitation wavelength.

ance of the TKER spectra obtained by TR-VMI are reassuringly consistent with those derived from HRA-PTS measurements at comparable photolysis wavelengths. The 260 nm image is obviously anisotropic, and well described by \(\beta = -0.5\). The higher TKER component of the 238 nm image also shows preferential perpendicular recoil (\(\beta \approx -0.25\)), while the signal at lower TKER appears isotropic. The images recorded at 200 nm is essentially isotropic.

The general form of each TKER spectrum is evident by \(\delta t = 500\) fs. Further changes out to \(\delta t = 50\) ps appear relatively modest, but the relative yield of low TKER products formed at both 238 nm and 200 nm clearly increase with increasing delay. This statement can be placed on a more quantitative footing by fitting the \(\delta t\) dependence of selected parts of the TKER signals obtained at each wavelength. Fig. 8 shows three such plots for products formed by (a) photolysis at 260 nm with TKERs in the range 0 - 8000 cm\(^{-1}\), and by 238 nm photolysis with TKERs in the range (b) 6000 - 11000 cm\(^{-1}\) and (c) 0 - 5000 cm\(^{-1}\). As in previous work,\(^{41}\) these transients were modelled using a combination of exponential rise and decay functions, convoluted with the IRF. Further details are included in the ESI. Fig. 8 simply shows the overall fit from which we obtained rise time constants \(\tau_{260} = 133 \pm 24\) fs, \(\tau_{238,\text{fast}} = 124 \pm 17\) fs and \(\tau_{238,\text{slow}} = 1.2 \pm 0.15\) ps, where fast and slow correspond to signal in the respective TKER ranges defined above. Similar analysis for the 200 nm data gives time constants, \(\tau_{200,\text{fast}} = 71 \pm 17\) fs, within the IRF, and \(\tau_{200,\text{slow}} = 4.7 \pm 1.3\) ps.

3.4 A plausible interpretation of the wavelength dependent fragmentation dynamics

The TR-VMI data serve to reinforce the main conclusions from the HRA-PTS studies. First, excitation of 2-thiophenethiol at long UV wavelengths (e.g. 260 nm) results in prompt formation of H atoms, with an anisotropic recoil velocity distribution. This is consistent with that expected in the event of S–H bond fission following dissociation on the \(\pi\sigma^*\) state PES. The R partner fragments are formed mainly in the first excited (\(\tilde{\chi}\)) electronic state, in the \(v=0\) level and in a spread of higher internal (vibrational) energy levels. Second, this prompt S–H bond fission process still operates at shorter wavelengths (e.g. 238 nm), but is supplemented by a secondary source of H atoms that appear at a slower rate, with lower kinetic energies and an isotropic angular distribution. Third, the H atom velocity distributions measured when exciting at yet shorter wavelengths (e.g. 220 nm and below) are quantitatively different. The recoil appears isotropic. The associated TKER spectra show no obvious signature of H + R(\(\tilde{\chi}\), \(v=0\)) product formation, peak at low TKER and extend to values compatible with one photon induced dissociation to H + R(\(\tilde{\chi}\)) products.

As noted above, the observations at long wavelength are con-
consistent with prompt S–H bond fission on the πσ* PES. The present data is not sufficient to determine whether this πσ* is populated directly, or via rapid radiationless transfer from the 1^1ππ* state. Given the ground state equilibrium geometry, Franck-Condon arguments dictate that the photoexcited 2-thiophenethiol molecules arrive on the excited state PES with their S–H bond pointing out of the ring plane. The H atom recoil anisotropy and, particularly, the deduced dominance of electronically excited (Å state) radical co-products imply that the photoexcited molecules remain sufficiently non-planar during S–H bond extension that they avoid CI-2 and follow the adiabatic path to products. We note many parallels between the present data and previously reported results for the near UV photolysis of 2-methyl-3-furanthiol.\textsuperscript{31} Obvious similarities include the respective ground state minimum equilibrium geometries, the near UV absorption spectra, the H atom recoil anisotropy, the appearance of the TKER spectra obtained when exciting at long wavelengths, and the respective S–H bond strengths obtained if one associates the prominent fast peak with formation of ground state radical products. Such an analysis led to a reported S–H bond dissociation energy for 2-methyl-3-furanthiol of 313 ± 100 cm\textsuperscript{-1}. No weak pedestal at higher TKER was identified in the earlier study\textsuperscript{31} but, given the present analysis, it appears more likely that near UV photolysis of 2-methyl-3-furanthiol results in a similar almost total population inversion between the Å and X states of the 2-methyl-3-furanthyl radical and that the previously reported (high) dissociation energy should actually be viewed as a threshold energy for forming Å state radical products.

The TR-VMI data for 2-thiophenethiol implicates some contribution from an alternative (slower) route to forming H atoms, with lower kinetic energies, once the excitation wavelength has decreased to 238 nm. The UV absorption spectrum (fig. 2), and its analysis based on the CASPT2 calculations (Table 1), suggest that most of the transition strength at this wavelength is provided by the 1^1ππ* ← S\textsubscript{0} excitation. Indeed, the observed photofragment energy disposal could be explained in terms of initial π* ← π excitation and subsequent radiationless transfer to, and dissociation on, the πσ* and S\textsubscript{0} PESs. The 238 nm TKER spectrum does not show an obvious step change from those measured at longer excitation wavelengths, suggesting that dissociation via coupling to the πσ* PES remains the major fragmentation pathway. However, the increased yield of slow, isotropic H atom products revealed by fig. 7(b) hints at the onset of a rival decay channel. This alternative channel most likely occurs following internal conversion to the S\textsubscript{0} state.

We have not conducted an exhaustive search for all possible low energy CIs between the ππ* and S\textsubscript{0} PESs, but have computed PECs for the ground and first few excited singlet states along the C\textsubscript{2}–S\textsubscript{1} bond extension coordinate, and calculated the relative energies of various parent isomers, transition states and fragmentation limits on the ground state PES. Fig. 9 shows the former PECs calculated (at the CASPT(2)/cc-pVDZ level) by systematic extension of R\textsubscript{C2–S1} and, at each step, allowing the rest of the ground state structure to relax to its minimum energy geometry (black filled points). The first three singlet excited state PECs were then calculated for this sequence of relaxed S\textsubscript{0} geometries.
Fig. 9 PECs along $R_{C-S}$ calculated at the CASPT2(10/8)/cc-pVDZ level of theory for the ground state and first three singlet excited states of 2-thiophenethiol. The filled circles show a relaxed scan along the $S_1$ PES. The open coloured circles show the excited state potentials calculated at these relaxed geometries. The solid red points are from a relaxed scan along the $S_1$ PES, with geometry optimisations performed the ADC(2)/cc-pVDZ level of theory and energy corrections at the CASPT2(10/8)/cc-pVDZ level; the open black points show the $S_0$ state energies calculated at these relaxed $S_1$ geometries.

and are shown by the open circles. The equivalent relaxed scan of the $S_1$ PEC from its optimised minimum energy geometry in the Franck-Condon region to longer C2–S1 bond lengths is shown by the filled red points. The open black points show the $S_0$ energies at these optimised $S_1$ geometries. One key finding from these calculations is the relative instability of one of the lower lying excited states with respect to $R_{C-S}$. The calculated PEC for this state shows a CI with the $S_0$ state at extended $R_{C-S}$ (henceforth termed CI-3), that is reminiscent of those identified for several other S (and O) containing heterocycles. Thus it is tempting to associate the additional yield of slower H atoms revealed in fig. 7(b) with population of this state (either directly, or by coupling from the $1\pi\sigma^*$ state), C2–S1 bond extension towards CI-3, radiative transfer to high vibrational levels of the $S_0$ state and subsequent unimolecular decay.

As fig. 10 shows, 2-thiophenethiol is the minimum energy structure on the $S_0$ PES, but we also identify two families of ring-opened isomers: A follows directly from C2–S1 bond fission, while formation of the isomer (B) also requires a trans-→ cis-isomerisation around the C3–C4 bond. A, B, the transition state separating A and B, and the calculated thresholds for S–H bond fission all lie well below the energy of a 238 nm photon (5.2 eV). Thus our favoured explanation for the additional yield of slower H atoms revealed in fig. 7(b) is unimolecular decay from highly vibrationally excited $S_0$ molecules. Both the minimal difference in the TKER distributions obtained by TR-VM at $\delta\tau = 500$ fs and 50 ps, and the clear showing of the TKER$_{max}$ peak in the HRA-PTS spectrum, implies that this is a minor channel at $\lambda_{phot} = 238$ nm.

The form of the spectra derived at shorter $\lambda_{phot}$ are very different, however, with no fine structure attributable to the H + R($\tilde{A}$, $\nu=0$) products and a high energy tail extending to TKER values compatible with H + R($\tilde{X}$, $\nu=0$) products. The 200 nm TR-VM data (fig. 7(c)) shows that these translationally excited H atoms are formed within 500 fs, and fig. 2 shows that the parent absorption cross-section increases further at these short wavelengths. Given these facts, the most plausible explanation for the short wavelength data involves excitation to one or more higher excited states, rapid radiationless transfer to the same $1\pi\sigma^*$ state as at longer excitation wavelengths, but with geometries sufficiently close to planar that some significant fraction of the dissociating flux now follows the diabatic path through CI-3 to H + R($\tilde{X}$) products.

The 200 nm TR-VM data (fig. 7(c)) shows formation of some H atom products with low TKER over a longer timescale. As at 238 nm, we attribute these products to the unimolecular decay of highly vibrationally excited $S_0$ molecules. The nature of the partner fragment is unclear from the present data. R, C and D would all be possible on energetic grounds. Density of states arguments would tend to favour R + H products, but the extent to which RRKM-like considerations should apply is unclear, given that the deduced unimolecular decay rate (even at 238 nm) exceeds the likely timescale for intramolecular energy randomisation on the $S_0$ PES.

4 Conclusions

This report details a combined PTS and ab initio study of H atom formation processes following near UV excitation of 2-thiophenethiol. The long wavelength (277.5 nm $\leq \lambda_{phot} \leq 240$ nm) PTS data (TKER spectra and recoil anisotropy measurements) are consistent with S–H bond dissociation after population of the lowest $1\pi\sigma^*$ PES. The thiophenethyl (R) radicals partnersing the observed H atoms are formed almost exclusively in their first excited $A^2A'$ state, but the observation of a weak pedestal attributable to H + R($\tilde{X}^2A'$) products allows determination of the S–H bond strength, $D_0 = 27800 \pm 100$ cm$^{-1}$ and the $\tilde{X}$–$\tilde{X}$ state splitting in the thiophenethyl radical ($\Delta E = 3580 \pm 100$ cm$^{-1}$). The finding of a large population inversion between the electronic states of the radical is viewed as a natural consequence of the non-planar ground state geometry, wherein the S–H bond is aligned almost at right angles to the ring plane. The obvious parallels between the present data and that reported previously following UV photodissociation of 2-methyl-3-furanthiol has led to a reinterpretation of the earlier data.

At shorter excitation wavelengths, $\pi^* \rightarrow \pi$ absorption dominates and the PTS spectra reveal, first, small changes ($\lambda_{phot} = 238$ nm) and then, more substantial changes once $\lambda_{phot} \leq 220$ nm. The former - a modest, longer-time build up of slow H atom products - is attributed to the onset of a rival internal conversion pathway to the $S_0$ PES via a CI (CI-3) accessed by extending the C2–S1 intra-ring bond. The more striking changes in the TKER spectra observed when photolysing at shorter wavelengths, in contrast, are attributed to excited state photochemistry: the excited states populated at these short wavelengths are deduced to rapidly predissociate, by coupling to the same $1\pi\sigma^*$ state that drives photofragmentation at longer wavelengths. In the short wavelength case, however, the dissociating molecules appear to attain sufficiently near-planar geometries en route to CI-2 to enable dissociation to the H + R($\tilde{X}$) products.

The recent literature contains a growing body of experimen-
Fig. 10 Calculated relative energies of 2-thiophenethiol, the biradical intermediate A formed upon C2–S1 bond fission, the lowest TS leading to the ring-opened isomers (B), selected H + radical (C, D, R) product limits and the lowest three body dissociation limit yielding two H atom products plus E. The various structures and products are shown to the right, along with their energies or threshold formation energies (in eV, defined relative to the ground state minimum). We have not checked for the presence (or otherwise) of barriers in the various fragmentation paths; the dashed lines simply correlate given structures to particular dissociation products. The horizontal dashed line indicates the total energy reached upon absorption of a 238 nm photon.
tal evidence for near UV photoinduced ring opening in similar heterocycles, in both the gas\textsuperscript{37,51–53} and condensed\textsuperscript{36,54} phases. The present investigations of the near UV photochemistry of 2-thiophenethiol invoke a (relatively minor) role for intra-ring C–S bond extension as a route to channelling excited state population back to the S\textsubscript{0} state, but provide no definitive evidence that full ring opening is able to compete with (fast) S–H bond fission.

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