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Electronic Supplementary Information to accompany

Extreme population inversion in the fragments formed by UV photoinduced S–H bond fission in 2-thiophenethiol

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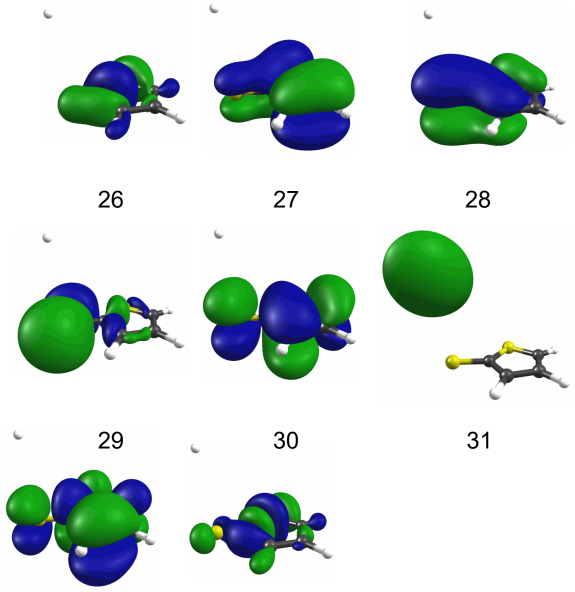
Vibrational Wavenumber Calculations for 2-thiophenethiyl Radical

Table S.1: Harmonic and anharmonic normal mode wavenumbers calculated at the B3LYP/6-311G(d,p) level for the ground state of the 2-thiophenethiyl radical. Modes are numbered in Herzberg notation.

Mode	Harmonic / cm^{-1}	Anharmonic / cm^{-1}	Symmetry
ν_1	3234	3088	A$'$
ν_2	3221	3078	A$'$
ν_3	3203	3061	A$'$
ν_4	1467	1432	A$'$
ν_5	1427	1398	A$'$
ν_6	1314	1288	A$'$
ν_7	1198	1173	A$'$
ν_8	1117	1099	A$'$
ν_9	1092	1075	A$'$
ν_{10}	990	972	A$'$
ν_{11}	854	838	A$'$
ν_{12}	710	696	A$'$
ν_{13}	622	609	A$'$
ν_{14}	453	449	A$'$
ν_{15}	261	260	A$'$
ν_{16}	930	906	A$''$
ν_{17}	834	813	A$''$
ν_{18}	710	684	A$''$
ν_{19}	567	559	A$''$
ν_{20}	458	450	A$''$
ν_{21}	193	188	A$''$

CAS Active Spaces

Figure S.1: Active orbitals included in CASSCF calculations along $R_{\text{S-H}}$, numbered in order of increasing energy. The HOMO is orbital 30



26 27 28

29 30 31

32 33

Figure S.2: Larger active space used for CASSCF calculations of transition dipole moments, oscillator strengths and vertical excitation energies. Orbitals are numbered in order of increasing energy. The HOMO is orbital 30

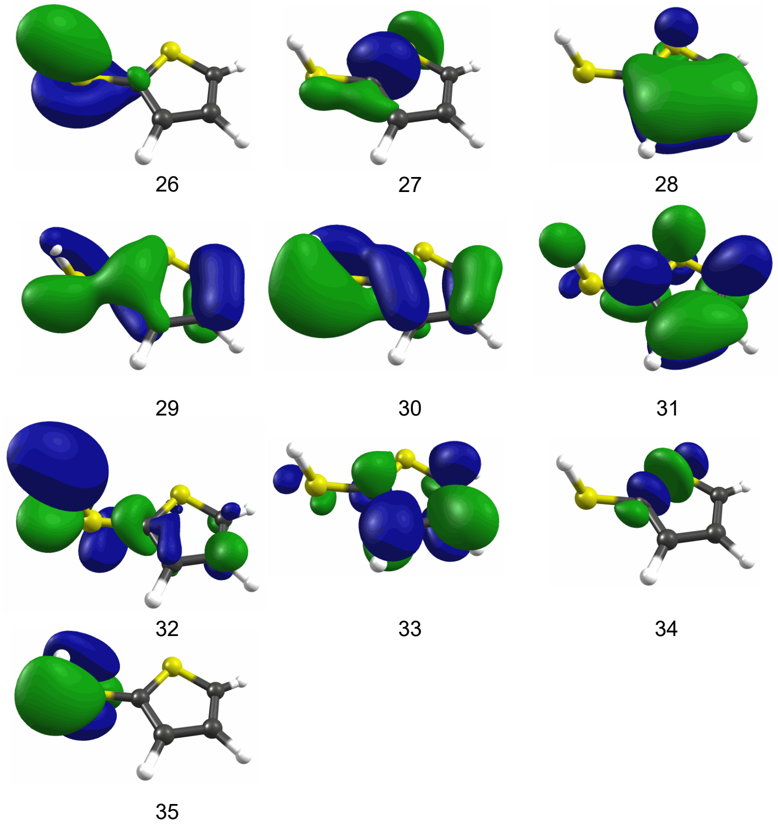


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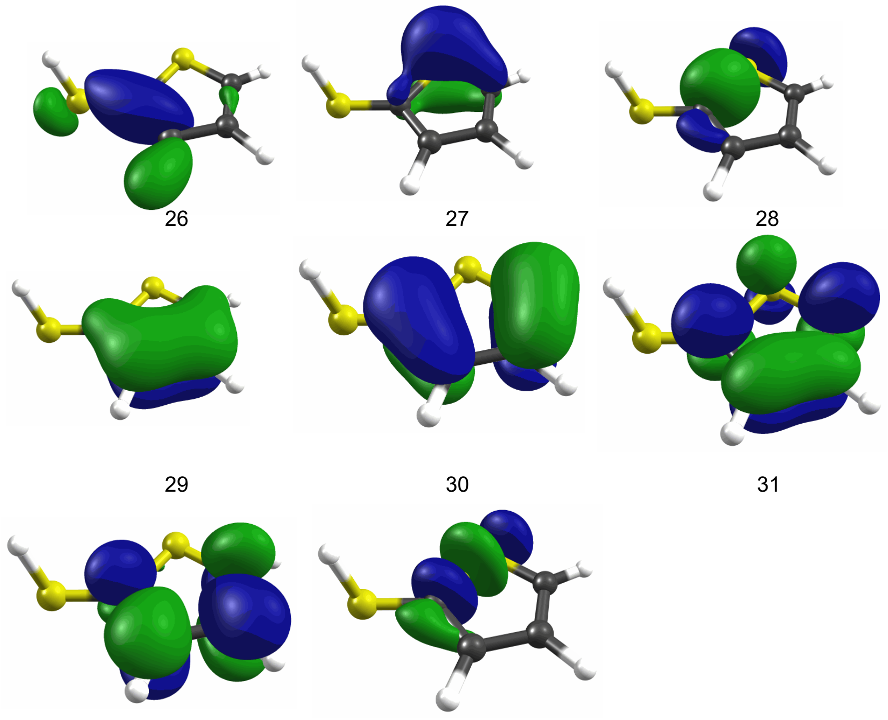
Figure S.3: 10/8 active orbitals included in CASSCF calculations along $R_{\text{C-S}}$ Orbitals are numbered in order of increasing energy. The HOMO is orbital 30



26 27 28

29 30 31

32 33

Kinetic modelling of the H^+ signal transients

H^+ signal transients obtained from time-resolved velocity map ion imaging (TR-VMI) measurements are modelled using a combination of exponential rise and decay functions, which are convoluted with the Gaussian instrument response function, $g(\Delta t)$.

We use a combination of: (i) a series of exponential rises, $f_n(\Delta t)$, which describe the rise in signal at $\Delta t > 0$ attributed to probed H-atoms generated through dissociation of the parent molecule; (ii) an exponential decay, $d(\Delta t)$, which accounts for the sharp 'spike' in signal around $\Delta t = 0$; and (iii) a second exponential rise function at $\Delta t < 0$, $r(\Delta t)$, which models the 'reverse dynamics' observed at all photoexcitation wavelengths. These functions are each convoluted with the Gaussian instrument response function, $g(\Delta t)$, and have the forms:

$$f_n(\Delta t) = g(\Delta t) * \left[1 - A_n \exp(-\frac{\Delta t}{\tau_{fn}})\right]$$

$$d(\Delta t) = g(\Delta t) * \left[B \exp(-\frac{\Delta t}{\tau_d})\right]$$

$$r(\Delta t) = g(\Delta t) * \left[1 - C \exp(-\frac{\Delta t}{\tau_r})\right]$$

where A_n, B and C are the amplitudes of each function, τ_f, τ_d and τ_r are the time-constants associated with each exponential function and Δt is the pump-probe time delay. The overall fit is subsequently given as:

$$a(\Delta t) = \textstyle\sum_n f_n(\Delta t) + d(\Delta t) + r(\Delta t)$$

where n is the minimum number of rise functions necessary to fit the data accurately.

Component fits presented in Figure 8 of the main manuscript have corresponding time-constants given as follows: (a) $\tau_{260} = 133 \pm 24$ fs; (b) $\tau_{238,\mathrm{fast}} = 124 \pm 17$ fs; and (c) $\tau_{238,\mathrm{slow}} = 1.2 \pm 0.15$ ps, with $\tau_d < 30$ fs and $\tau_r < 30$ fs (see below).

Explanation of reverse dynamics of the H^+ signal transients

The reverse dynamics observed in the H^+ signal transients correspond to single photon excitation with 243 nm, forming H-atoms which are then two-photon excited with 243 nm to the $2s$ level and subsequently ionised with a single photon of the pump laser to yield H^+ ions. Precedence for such an explanation has been set in previous work by Roberts *et al.*[1] and Lippert *et al.*[2] Photodissociation to yield H-atoms and two-photon excitation of the $2s \leftarrow 1s$ transition all needs to occur, therefore, within the temporal width of the 243 nm pulse (80 fs), hence giving rise to the very fast time-constant of $\tau_r < 30$ fs (see above).

1. G. M. Roberts, C. A. Williams, H. Yu, A. S. Chatterley, J. D. Young, S. Ullrich and V. G. Stavros, *Faraday Discuss.*, 2013, **163**, 95–116
2. H. Lippert, H. H. Ritze, I. V. Hertel and W. Radloff, *ChemPhysChem*, 2004, **5**, 1423–1427