Time-resolved Photoelectron Spectroscopy Study of Halothiophene Photochemistry

Contact *r.s.minns@soton.ac.uk*

W. O. Razmus, H. J. Thompson and R. S. Minns

School of Chemistry and Chemical Engineering
University of Southampton, Southampton, UK, SO17 1BJ

M. A. Parkes

Department of Chemistry
UCL, London, UK, WC1H 0AJ

E. Springate, R. T. Chapman, Y. Zhang, J. O. F. Thompson

Central Laser Facility
RAL, Didcot, UK OX11 0QX

Introduction

Thiophene is a heterocyclic ring with a Sulphur atom at the 1 position and forms a key chemical constituent in a wide number of photoactive systems and organic semiconductor materials.[1] Recent studies have shown that by varying the substituents on the ring one can change the photoactive mechanisms, leading to the formation of different products. For example, experiments on thiophenone, where a pendular carbonyl group is attached to the ring, show that following UV excitation ultrafast ring opening occurs.[2] Conversely, addition of a pendular halogen (X), has been shown to lead to rapid dissociation of the C-X bond.[3-5] There has been significant discussion in the literature to see if this occurs in conjunction with any ring opening processes, but this remains as yet unknown.

Previous measurements have shown that at pump wavelengths around 266 nm, the excitation is dominated by population of the dissociative $(\boldsymbol{n}/\boldsymbol{\pi})\boldsymbol{\sigma}^*$ states localized on the C-I bond leading to rapid dissociation of the C-I bond.[5] Nanosecond measurements of product state momentum distributions suggested that as the pump wavelength is tuned to the blue the relative importance of excitation into the $\boldsymbol{\pi\pi}^*$ state increases reaching a maximum around 245 nm, and that this may lead to a higher propensity for ring opening.[4] However, no time-resolved measurements have been performed at such wavelengths.

In recent experiments at Artemis we have used femtosecond time-resolved photoelectron spectroscopy to study 2-iodo and 2-bromo thiophene at 266 nm and 245 nm to compare the dynamics how the character of the initial state populated affects the ensuing dynamics. Here we only report on the 2-iodothiophene.

Experimental

The experiment was performed at the Artemis laser facility at the Rutherford Appleton Laboratory in Didcot, UK. The method has been described previously[6] such that brief details are provided here. The pump and probe pulses are generated from the output of a 1 kHz Ti:Sapphire chirped pulse amplification (CPA) laser system operating at 800 nm. The output is split providing two separately compressed pulses with durations of approximately 30 fs. The UV pump is generated via a high energy OPA, producing wavelengths of 245 nm and 262 nm at pulse energies up to 10 uJ.

For the probe pulse, a 400 nm beam was obtained by frequency doubling the 800 nm output of the CPA system. Approximately 300 uJ of the 400 nm light was then focused into a jet of argon gas for HHG. A single harmonic, with an energy of ~ 22 eV, was selected using the time-preserving monochromator,[7] and this was then focused into the interaction region with a torodial mirror.

The photoelectrons were detected in an electron time of flight detector providing a resolution of $T/\Delta T \sim 100$, corresponding to an energy resolution on the order of 0.1 eV for electrons with kinetic energies around 10 eV.

A translation stage in the pump beam path was used to change the pump-probe time delay.

The 2-iodothiophene sample was contained in a liquid sample holder, and He was used as a carrier gas to introduce it to the interaction region through a nozzle.

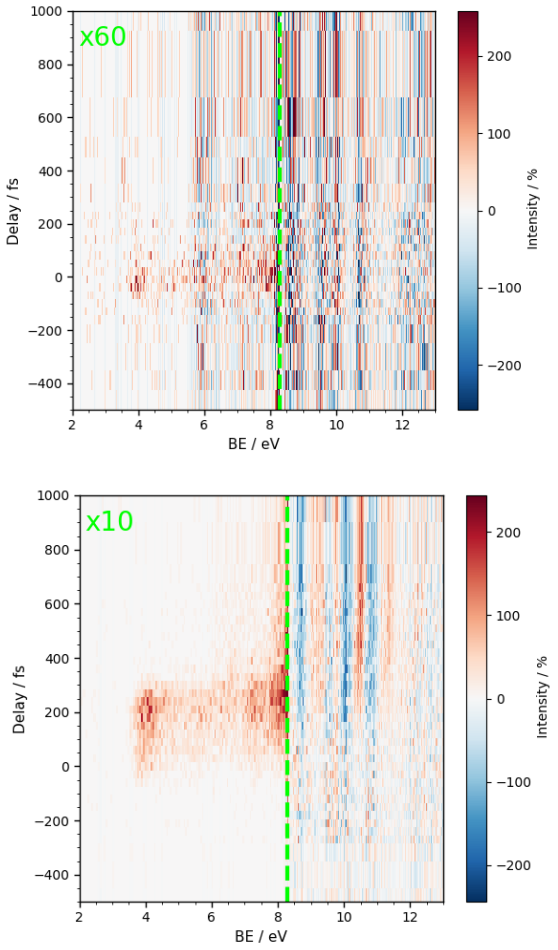

Figure 1. Difference photoelectron heatmap of 2-iodothiophene following photolysis at 262 nm (top) and 245 nm (bottom). The intensity on the left-hand side of the green dashed line is multiplied by a scaling factor, as defined in the figure, to make the lower intensity excited state signals clearer.

Results and Discussion

In figure 1 we present the background subtracted heatmap associated with the measurements of 2-iodothiophene pumped at 262 nm (top) and 245 nm (bottom). In each case, the ground state background spectrum obtained at delays pre-time-zero have been subtracted to obtain a differential map of the photoelectron intensity as a function of delay and binding energy (BE). The plots show clear differences in both signal intensity and temporal characteristics. Considering the signal levels first, the absorption

spectrum peaks around 240 nm where the excitation is dominated by population of the $\pi\pi^*$ excited state with at most a very minor contribution from direct excitation in the manifold of $(n/\pi)\sigma^*$ states. At 245 nm this remains true, and the absorption cross-section remains high. At 262 nm, the absorption cross section has dropped by approximately an order of magnitude and the excitation is now dominated by transitions into the $(n/\pi)\sigma^*$ manifold of states.[5]

The differences in character of the initially excited state are also evident in the time-dependence of the signal. Excitation into the $(n/\pi)\sigma^*$ leads to rapid breading of the C-I bond and the formation of the thiophenyl radical and atomic iodine fragments. In accord with previous measurements this process occurs on an ultrafast timescale. While the signal contrast in the measurement at 262 nm are not sufficient to see the iodine fragments that are formed, we can see the excited state signal decay extremely rapidly and the C-I bond breaks. In figure 2, we plot the integrated intensity associated with the excited state signal over the binding energy ranges 3.8-4.2 eV and 7.25-8.0 eV. The 3.8-4.2 eV energy range is associated with molecules in their initially excited state at the Franck-Condon geometry. The signal is seen to fall back to baseline levels within 100 fs with the signal shifting to higher binding energies as the C-I bond length increases, as seen in analogous systems like methyl iodide.[8,9] At higher binding energies around 7.25-8.0 eV we see a slightly delayed appearance and similar ultrafast decay as the molecule transitions to separated fragments. There is potentially a weak, long-lived signal seen in this region which could be associated with the thiophenyl radical product which is expected to have an ionization potential around 8 eV.[5]

The data at 262 nm is therefore consistent with previous measurements performed with other probes that show the dynamics are dominated by rapid dissociation of the C-I bond.

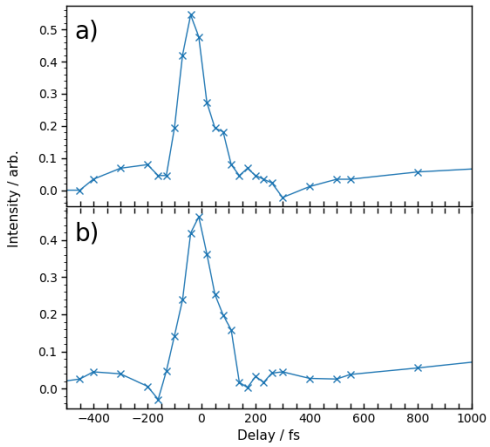

Figure 2. Total difference photoelectron intensities over the energy ranges 3.8-4.2 eV (a) and 7.25-8.0 eV (b) following photolysis of 2-iodothiophene with a 262 nm laser pulse.

The data associated with a pump wavelength of 245 nm show quite different characteristics. The higher excitation cross-section means we can also see the products formed that overlap with the ground state signal. The integrated intensity over the same excited state regions are plotted in figure 3 a) and b), along with signals associated with the two spin orbit states of iodine in c) and d).

Focusing on the excited state signals first, the initial region associated with the Franck-Condon geometry shows a rapid rise at time zero but reaches a secondary, higher intensity, maximum after approximately 200 fs. This increase in intensity coincides with a shift in energy seen in the photoelectron spectrum shown in figure 1. We assign this change in intensity and spectrum with a geometry change in the $\pi\pi^*$ populated. Preliminary calculations indicate this relates to an expansion of the ring. The signal then decays in intensity, and we see a similar shift to higher binding energies as seen with the 262 nm pump. This manifests in the spectrum as a delayed intensity maximum being reached in the 7.2-8 eV region of the spectrum. The much higher signal levels also allow us to identify the long-lived signature of the thiophenyl radical in this energy region.

The iodine products are seen to rise on the timescale of the removal of the excited state signal with no discernable difference between the formation of the two spin orbit states. The iodine signals are fit to an error function with a variable time-zero to characterize the formation time of the products. This provides a value of 250 fs for the centre of the rise and is marked in the figure by a dashed line.

While we do not see the products formed in the 262 nm data, we can infer that the formation of the iodine fragments occurs on a significantly faster timescale such that the geometry changes and internal conversion in the 245 nm data leads to a delay in formation.

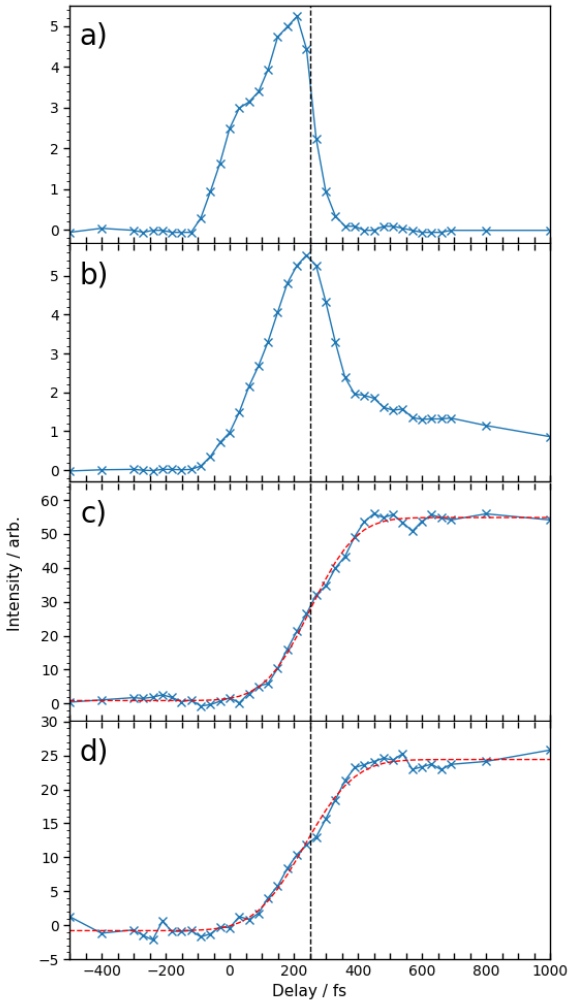

Figure 3. Total difference photoelectron intensities over the energy regions: 3.8-4.2 eV (a), 7.25-8.0 eV (b), 10.38-10.53 eV (c) and 11.2-11.45 eV (d). The measured intensities are shown in blue with "x" marking the data points and fits in panels c) and d) are shown as red dashed lines. A vertical dashed line marks the centre of rise calculated in the fit.

One final thing to note is that there is no sign of any ring-opening occurring at either wavelength. In analogy with the work on thiophenone,[2] we would expect such processes to lead to a broad photoelectron band at binding energies below that of the thiophenyl radical. The absence of this suggests that ring opening is a very minor channel at best for iodothiophene at the wavelengths studied.

Conclusions

Time-resolved photoelectron spectroscopy measurements of 2-iodothiophene have been performed using an extreme ultraviolet probe. Measurements at 245 nm and 262 nm show quite different dynamics deriving from the differences in the character of the initially excited states.

At 262 nm, excitation of $(\boldsymbol{n}/\boldsymbol{\pi})\boldsymbol{\sigma}^*$ states leads to rapid dissociation of the C-I bond. At 245 nm, excitation of the $\boldsymbol{\pi\pi}^*$ state leads to structural changes, before internal conversion onto the $(\boldsymbol{n}/\boldsymbol{\pi})\boldsymbol{\sigma}^*$ states and C-I bond cleavage. At both wavelengths studied there is no sign of any significant ring opening channel over the timescales measured.

Acknowledgements

We wish to thank Phil Rice and Ace Cox for technical assistance during the experiment.

References

1. *Handbook of Thiophene Based Materials: Applications in Organic Electronics and Photonics*, ed Perepichka and Perepichka, John Wiley and sons ltd, Chichester, UK 2007
2. Pathak, *et al*. Nat. Chem. **12**, 795 (2020)
3. Marchetti *et al*. J. Chem. Phys. **142**, 224303 (2015)
4. Toulson *et al*. J. Chem. Phys. **159**, 034304 (2023)
5. Razmus *et al*. Phys. Chem. Chem. Phys., **26**, 12725 (2024)
6. Smith *et al*. Phys. Rev. Lett. **120**, 183003 (2018)
7. Frassetto *et al*. Opt. Express **19**, 19169 (2011).
8. Downes-Ward *et al*. J. Phys. B. **54**, 134003 (2021)
9. Warne *et al*. Phys. Chem. Chem. Phys. **22**, 25695 (2020)