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# Probing Delayed C–I Bond Fission in the UV Photochemistry of 2-Iodothiophene with Core-to-Valence Transient Absorption Spectroscopy

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**Abstract:** The UV photodissociation dynamics of 2-iodothiophene are monitored by an XUV probe pulse that promotes iodine 4d core-to-valence transitions. Absorption changes from molecular iodine species conclusively show that dissociation requires up to ~1 picosecond. © 2020 The Author(s)

## 1. Introduction

Photoprotective behavior is exhibited by molecules such as DNA bases and sunscreen, wherein a photoexcited molecule can convert absorbed photon energy into benign thermal excitation through coupled electronic and nuclear dynamics and interaction with the environment.[1] An alternative fate is photodamage, where bond fission can lead to ring-opening and photofragmentation. The experimental and theoretical understanding of photoinitiated heterocyclic ring-opening have been surveyed recently.[2] In particular, for sulfur-containing compounds the importance of triplet states in their photochemistry is gaining recognition, as intersystem crossing (ISC) can significantly perturb the dynamics and number of surface crossings.[3]–[5] Here, we probe electronic structure changes during UV-induced dissociation of 2-iodothiophene from the perspective of the iodine atom in search of evidence for ring-opening as a precursor to fragmentation.

## 2. Experimental Method

Experiments are performed using a femtosecond XUV transient absorption setup that has been described previously.[6], [7] XUV pulses are produced using high-harmonic generation (HHG) and filtered from the NIR driving laser using an aluminum foil. The XUV is focused into a ~4 mm long sample cell containing 2-iodothiophene. The transmitted XUV is detected by a spectrometer consisting of a variable line-space grating and an X-ray CCD camera. Transient absorption spectra are measured by introducing a UV pump pulse into the sample cell with variable time delay relative to the XUV probe pulse. The UV-induced change in absorbance is calculated for each time delay  $\Delta t$  as  $\Delta A = -\log_{10}(I_{\text{pump-on}}/I_{\text{pump-off}})$  where  $I_{\text{pump-on}}$  is the XUV spectrum recorded in the presence of the pump beam, while  $I_{\text{pump-off}}$  is recorded with the pump beam blocked by a chopper wheel.

## 3. Results and Discussion

The transient absorption spectra shown in Fig. 1A are obtained by integrating the measured  $\Delta A(E, \Delta t)$  over separate pump-probe time-delay ranges as indicated in the figure legend. To guide assignment of the numerous sharp absorption features, literature  $np \leftarrow 4d$  absorbance for both iodine atoms and ions are shown at the top of the figure, as a stick spectrum and after Gaussian convolution.[8] Neutral I atoms are probed by  $4d^9 5s^2 5p^6 \leftarrow 4d^{10} 5s^2 5p^5$  core-to-valence excitations, where both the core and valence orbital energies are split by spin-orbit coupling. Ground state I atoms are probed by  $^2D_{5/2} \leftarrow ^2P_{3/2}$  and  $^2D_{3/2} \leftarrow ^2P_{3/2}$  transitions into spin-orbit-split core-excited states at 45.94 eV and 47.64 eV, respectively, while (valence) spin-orbit excited I\* atoms are observed by the  $^2D_{3/2} \leftarrow ^2P_{1/2}$  transition at 46.70 eV.[8] Depletion of the parent molecule concentration by UV pump excitation is observed as a negative change in absorbance beyond ~50 eV, owing to transitions from the iodine core  $4d_{5/2}$  and  $4d_{3/2}$  orbitals into  $\sigma^*$  and  $6p$  orbitals, forming broad absorption features.

The time-dependent behavior of the XUV transient absorption spectra is explored in Fig. 1B by inspecting key spectral regions using the same colors as marked by color-coded bars in Fig. 1A. The circular data points in Fig. 2B are obtained by integrating the time-dependent signals (indicated by the width of the horizontal bars) and their respective maxima are normalized. Solid curves are the result of a global fit procedure. The time-dependent depletion of the parent 2-iodothiophene population near 51 eV is shown in black. An important observation is that following UV excitation, the 2-iodothiophene population bleach continues to increase up to delays of  $\sim 1$  ps. Absorption changes in this energy window correspond to molecular, rather than atomic, iodine species and conclusively show that the dissociation is not yet complete. This conclusion is further supported by the delayed appearance of neutral I atoms, beginning to rise only after  $\sim 100$  fs have elapsed and gradual changes in the asymptotic yield can be seen up until  $\sim 1$  ps. A global model allows overlapping spectral features of the time-resolved spectra to be decomposed into their transient spectral contributions. Spectral signatures of ring closed vs. ring open dissociation pathways will be explored through comparison with *ab initio* core absorption spectra, in combination with molecular dynamics calculations, to unlock a detailed atomic-scale picture of the dissociation dynamics.

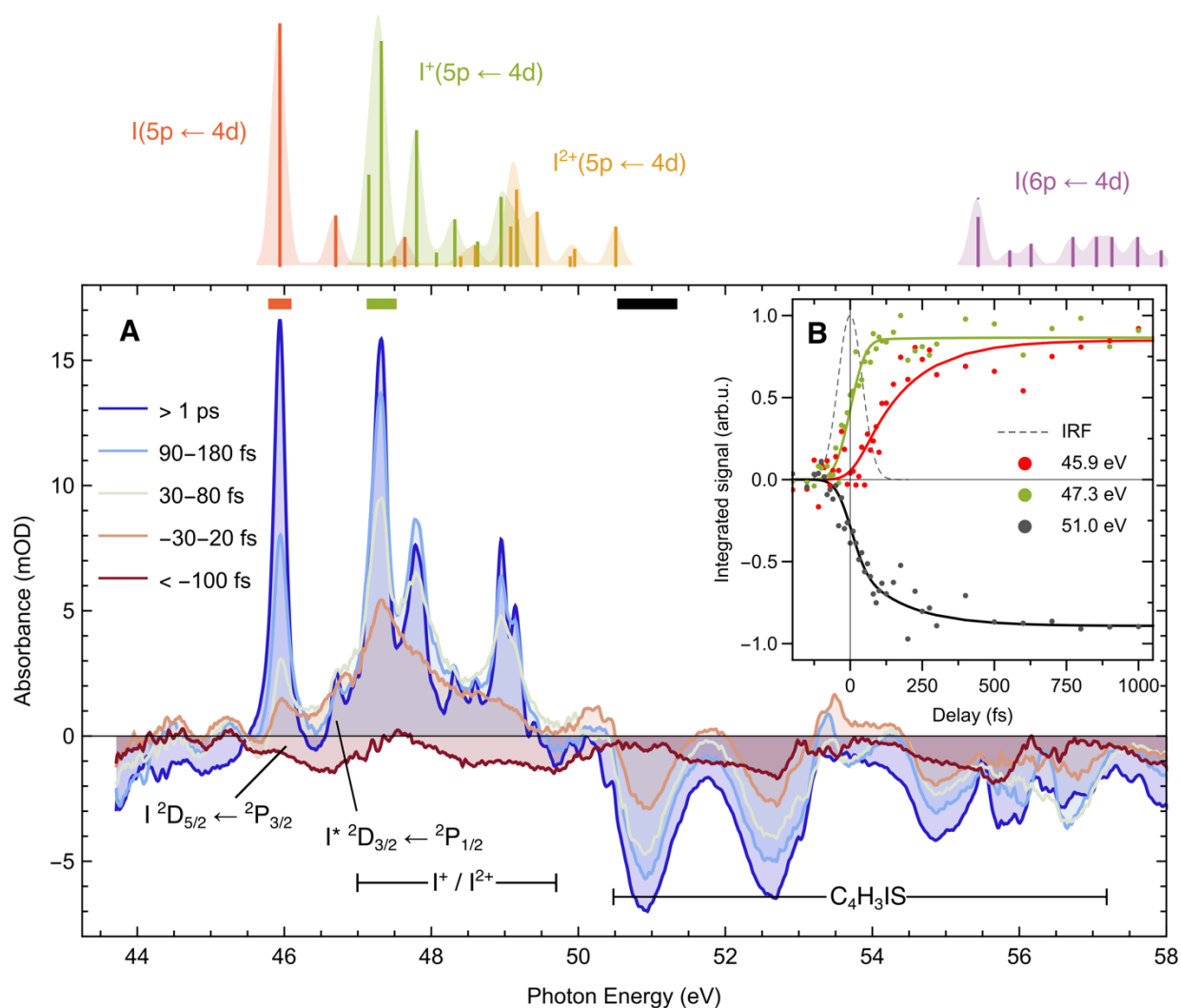


Figure 1. (A) UV pump – XUV probe transient absorption spectra at the iodine 4d edge of 2-iodothiophene. Negative-going signal at energies  $>50$  eV corresponds to depletion of the parent molecule. At very early times  $[-30\text{--}+20]$  fs (blue), a broad feature associated with a short-lived species near 48 eV is observed, at intermediate delays  $[90\text{--}180]$  fs (red), pronounced asymmetry in the neutral I atom near 46 eV is observed, while after  $>1$  ps (black) the asymptotic products are formed. Color-coded bars indicate the energies selected to illustrate time-dependent spectral trends in panel B. (B) Circular points are measured data using the same color codes (energies specified in legend). The solid lines correspond to the result of a global fit analysis. The instrument response function (IRF) measured in xenon is overlaid (dashed gray). Literature  $np \leftarrow 4d$  absorbance spectra for both iodine atoms and ions are shown at the top of the figure, as a stick spectrum and after Gaussian convolution.[8]

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