Ultrafast dynamics through conical intersections and intramolecular vibrational energy redistribution in styrene

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Abstract

We report a femtosecond time-resolved photoelectron spectroscopy (TRPES) investigation of internal conversion in the first two excited singlet electronic states of styrene. We find that radiationless decay through an S_1/S_0 conical intersection occurs on a timescale of ~ 4 ps following direct excitation to S_1 with 0.6 eV excess energy, but that the same process is significantly slower (~ 20 ps) if it follows internal conversion from S_2 to S_1 after excitation to S_2 with 0.3 eV excess energy (0.9 eV excess energy in S_1).

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1. Introduction

Ultrafast relaxation of electronic excited states through conical intersections plays a significant role in many photochemical and photobiological processes. There are many examples of photochemical isomerisations about C=C double bonds that have been shown to involve conical intersections,¹ and styrene has been studied as a prototype for these processes, despite the fact that the two unsubstituted styrene isomers are equivalent. Styrene can also be considered as a substituted benzene, and therefore the electronic relaxation pathways can be expected to have similarities with those of benzene.

The gas-phase ultraviolet (UV) absorption spectrum of styrene in the region up to around 7 eV consists of three main bands.² Historically, there was some debate over the electronic origin of the second band, with most early studies assuming that it arose from excitation to both S_2 and S_3 ;³⁻⁴ however, it is now generally accepted that the first two bands arise from excitation to the lowest two singlet electronic states, S_1 and S_2 , and result from excitations within the valence π - π^* molecular orbitals.⁵⁻⁶ The zero-points of the S_1 and S_2 states have been determined spectroscopically to be 4.31 eV⁷ and 4.88 eV,⁸ respectively.

Philis *et al.*,^{2,9} observed the 3p Rydberg states of styrene at 6.259 eV, 6.456 eV and 6.529 eV by resonance-enhanced multiphoton ionisation (REMPI), assigned them $3p_y$, $3p_x$ and $3p_z$ by comparison with CASPT2 calculations,⁵ and determined lower limits for their lifetimes of 91 fs, 38 fs and 165 fs from linewidth measurements. The absorption coefficients of these Rydberg states are small and their involvement in the photochemistry of styrene has not been reported as significant.

Energy barriers to decay on the S_1 surface can be estimated from vibronic spectroscopy experiments and for isolated styrene and β -methylstyrene have been found to be at least 3000 cm⁻¹ above the S_1 origin.¹⁰⁻¹² Phosphorescence has never been detected from photoexcited styrene; however, many studies have suggested that photochemical *cis-trans* isomerisation mechanisms for styrene proceed *via* triplet states.^{11, 13-15}

Recent theoretical studies have investigated the decay pathway of photoexcited S_2 styrene in some detail. According to Amatatsu,¹⁶ after passing through the S_2/S_1 conical intersection (CI) with a twisted quinoid geometry, population can either relax directly to the S_1 equilibrium structure or it can pass to a nearby transition state from where it can then relax to the S_1 equilibrium geometry and/or proceed on to an S_1/S_0 conical intersection. With insufficient vibrational excess energy, the only possible singlet decay mechanism from the S_1 equilibrium geometry is fluorescence, which is

known to have a nanosecond timescale. The only ultrafast decay pathway from S_1 is to S_0 directly *via* a conical intersection, requiring extra vibrational energy. Bearpark, Robb and coworkers have calculated two different S_1/S_0 CI geometries that could be important to S_1 decay¹³ and others have also been reported.¹⁷

In a systematic study of the decay dynamics of a number of substituted benzenes, Stolow and coworkers reported 52 fs S_2/S_1 decay followed by 88 ps S_1/S_0 decay in styrene excited at the S_2 origin.¹⁸ The motivation for our work was to investigate the decay dynamics of photoexcited styrene in more detail.

Experiments measuring the integrated ionisation cross-section as a function of pump-probe delay cannot differentiate between internal conversion (IC), intersystem crossing (ISC) or the possibility of either of these photophysical processes occurring in combination with photochemistry; particularly isomerisation in this case. The key to developing a detailed picture of the excited state dynamics in a prototypical system such as styrene, and to developing a detailed understanding of the excited state dynamics of any molecule, is to measure the electronic and nuclear composition of the total wave function of the molecule as it evolves. In practice, because the electronic and nuclear motions are strongly coupled, this is not trivial; however, time-resolved photoelectron spectroscopy (TRPES) has emerged as an extremely valuable tool for following excited state non-adiabatic processes in molecules.¹⁹⁻²² First, an ultrafast laser pulse (pump) prepares the molecule in an electronically and vibrationally excited non-stationary state, and then, a subsequent ultrafast laser pulse (probe) ionises the molecule and projects the evolving molecular wave function onto the molecular ionisation continuum. By measuring the resulting photoelectron spectrum as a function of pump-probe delay, one can gain some insight into the electronic and geometric changes along the reaction coordinate. TRPES has been employed to monitor wave packet dynamics in simple diatomic molecules,²³ to follow IC in polyenes,²⁴ photodissociation,²⁵⁻²⁷ intramolecular vibrational energy redistribution (IVR)²⁸ and ISC.^{26, 29-31} However, in molecules in which there is a high density of electronically excited states correlating to the same electronic state of the cation, decomposing the evolving wavefunction into its constituent parts is challenging, and requires the support of theory.

In this paper, we present femtosecond time-resolved photoelectron spectra of styrene collected using different pump wavelengths. The data have been analysed using an ionisation correlation analysis based on time-dependent density functional theory (TDDFT) calculations, and provides direct experimental evidence for decay *via* different singlet state photophysical pathways in styrene after excitation to S_1 and S_2 , as suggested by earlier calculations.^{13, 16}

2. Theory

The basic principles of our investigation of the excited state dynamics of styrene are illustrated schematically in figure 1. Immediately after excitation by the pump pulse, the total excited state wavefunction is a linear combination of vibronic wavefunctions, $\psi_i(q)e^{-iEt/\hbar}$, integrated over the envelope of the electric field, $\varepsilon(E)$: $\Psi(t) = \int dE \varepsilon(E) \sum_{i,q} c_i^q(t) \psi_i(q) \exp(-iEt/\hbar)$, where i labels the S_n electronic states, q represents the vibrational modes and $c_i^q(t)$ are the time-dependent amplitudes. The photoelectron spectrum of each of these electronic states can, in principle, be distinguished because they have different overlap integrals between their vibronic wavefunctions and those of the cation; however, the bands are strongly overlapping and not trivial to disentangle (see top right inset in figure 1).

In order to unravel the photoelectron spectrum it is necessary to identify which regions of the photoionisation continuum are associated with ionisation from the different S_n electronic states, *i.e.* we need to determine vibronic transition propensities between styrene and the styrene cation. To a first approximation, we can deduce the ionisation correlations at the Franck-Condon geometry and treat the electronic and vibrational components of the wavefunctions separately. For the vibrational component, if we assume that the vibrational quantum number is approximately preserved during photoionisation, we expect the photon energy threshold for ionisation out of S_3 to be lower than that from S_2 , which in turn is lower than that for S_1 (see figure 1). For the electronic component, we need to establish correlations between the electronic states of the neutral molecule and the electronic states of the cation.

To be able to determine the ionisation correlations at the Franck-Condon geometry, we have carried out quantum chemistry calculations for the electronically excited states of neutral styrene and its cation. The geometry of the ground state of neutral styrene was optimized at the DFT B3LYP/6-31G* level. The optimised geometry is planar, all the in-plane angles are approximately 120°, the CH distances are 1.09 Å, the CC bond lengths in the benzene ring are 1.40 Å, the ethylene CC bond is 1.34 Å and the CC bond joining the benzene ring to ethylene is 1.47 Å. This geometry was used for all other calculations.

Orbitals for the ground state wavefunctions of styrene and the styrene cation (calculated at the DFT HCTH/6-311+G* level) are the reference orbitals for the TDDFT HCTH/6-311+G* excited state calculations³²⁻³³ and are presented in figure 2. The resulting configurations and weights of the excited state wavefunctions for

styrene and the styrene cation are summarized in tables 1(a) and (b).^{*} Since our focus here is on experimental assignment, we have used experimental excitation energies instead of those calculated at this level of theory where possible. The TDDFT theory is used here to calculate the electronic state configuration and the correlations between the excited states of the neutral molecule and the cation as described below. The asymptotically corrected HCTH functional³²⁻³³ was chosen as it was found to give reliable excitation energies for benzene.³⁴

(a)	Energy (eV)	Excitation configuration from S_0	Coefficient	Weight
S_1	4.31 ⁷ (4.47)	HOMO-1→LUMO	0.48	0.45
		HOMO→LUMO	0.23	0.10
		HOMO→LUMO+1	-0.47	0.44
S_2	4.88 ⁸ (4.67)	HOMO-1→LUMO	-0.26	0.13
		HOMO→LUMO	0.64	0.82
S_3	6.19 ⁵ (5.31)	HOMO-2→LUMO+1	0.20	0.08
		HOMO-1→LUMO	0.41	0.34
		HOMO-1→LUMO+5	-0.15	0.04
		HOMO→LUMO	0.13	0.03
		HOMO→LUMO+1	0.49	0.47

(b)	Energy (eV)	Excitation configuration from D_0	Coefficient	Weight
D_0	8.46 ³⁵	Ground configuration		
D_1	9.12	HOMO-1→HOMO	1.00	1.00
D_2	10.76	HOMO-1→LUMO	0.18	0.03
		HOMO→LUMO	0.27	0.07
		HOMO-2→HOMO	0.94	0.88

Table 1 Energies and configurations of the lowest electronic states of styrene (a) and the styrene cation (b). The energies are all relative to S_0 . The configurations of the electronically excited states of styrene and the styrene cation were calculated at the TDDFT HCTH/6-311+G* level and are expressed in terms of the orbitals for the

^{*} For the excited states of the cation, the total spin of the wavefunction was not constrained; however, the expectation values of S^2 for the lowest five cation excited state wavefunctions were 0.75-0.78, corresponding to doublets.

ground state wavefunctions plotted in figure 2. (a) The values for the S_1 ⁷ and S_2 ⁸ energies are the experimentally determined band origins. For comparison, the values calculated at the TDDFT HCTH/6-311+G* level are given in brackets. The value for the S_3 energy is from a CASPT2 calculation⁵ which is more accurate than our calculated value. Due to the nature of the wavefunction from the TDDFT calculation, the sum of the squares of the configuration coefficients for each excited state is approximately 0.5 for neutral styrene. The values quoted for the weights are the squares of the coefficients, multiplied by a factor of 2. (b) The value for the D_0 energy relative to S_0 is the experimentally determined first ionisation potential.³⁵ The values for the D_1 and D_2 energies were obtained by adding our TDDFT HCTH/6-311+G* vertical excitation energies for the cation to this. The sum of the squares of the configuration coefficients for each excited state of the styrene cation is approximately 1.0. The values quoted for the weights are the squares of the coefficients. We have not found any experimental data with which to compare our TDDFT HCTH/6-311+G* calculated energies of D_1 and D_2 ; however, Stolow and coworkers calculated values of 10.65 eV and 10.94 eV at the TDDFT B3LYP/6-311+G* level¹⁸ which are similar.

One-electron ionisation correlations can be determined by inspection of tables 1(a) and (b). The electronic configuration of D_0 has a singly occupied highest occupied molecular orbital (HOMO, illustrated in figure 2) while the electronic configuration of D_1 has a lower energy singly occupied molecular orbital, labeled HOMO-1, and a pair of electrons in the HOMO. We approximate (based on table 1(b)) that the electronic configuration of D_2 corresponds to a single electron in HOMO-2 and a pair of electrons in each of HOMO and HOMO-1.

We assume that ionisation by ultraviolet light involves removing an electron in the highest energy orbital (Koopmans' approximation). From S_1 (table 1a), this implies an approximately equal probability for removing an electron from LUMO and LUMO+1: removal from LUMO would leave singly occupied HOMO-1, and correlates with the D_1 state for the cation; while removal from LUMO+1 would leave a singly occupied HOMO, corresponding to the cation D_0 state. Thus using Koopmans' approximation at fixed Franck Condon geometry, we correlate S_1 with the D_0 and D_1 states of the cation at different excitation energies, and S_2 almost exclusively with D_0 using the same method, while S_3 correlates with D_0 , D_1 and D_2 states of the cation. Approximate ionisation probabilities (not intensities) can be obtained by summing the weights of the neutral configurations that correlate with a particular electronic state of the cation, and these are listed in table 2.

Neutral state	Cation state	Approximate transition probability
S ₁	D ₀	0.5
	D ₁	0.5
S ₂	D ₀	0.8
	D ₁	0.1
S ₃	D ₀	0.5
	D ₁	0.4
	D ₂	0.1

Table 2 Approximate ionisation correlations between excited singlet states of styrene and the lowest doublet states of the styrene cation.

We assume that vibrational energy is conserved in the transition from the excited state to the cation. This assumption, together with the electronic correlations described above and summarized in table 2, allows approximate photoelectron band energies to be predicted between excited states, and thus the TRPES bands can be assigned to first order, as illustrated in figure 1. Such an approximate assignment method has been reported in the literature as an analysis tool for time-resolved photoionisation studies of styrene and other molecules^{18, 24, 29} and provides theoretical band energies that agree well with those observed.

3. Experiment

The experimental apparatus consists of a femtosecond laser system, molecular beam and velocity map imaging spectrometer. The commercial femtosecond laser system consists of an ultrafast oscillator and amplifier producing a 1 kHz train of 2.5 mJ pulses of 35 fs duration and a central wavelength of 795 nm. For most experiments, approximately 70% of the light from the amplifier pumps two optical parametric amplifiers (OPAs) to generate tunable infrared (IR) radiation between 1200 nm and 2000 nm. The signal from each OPA is then mixed with the residual pump light to produce visible light between 470 nm and 600 nm which is subsequently frequency doubled to produce light at 254 nm and 240 nm. The bandwidth of the UV light is 150-180 cm⁻¹. For some experiments, 35% of the light from the amplifier pumps one

OPA and 35% of the light from the amplifier is frequency-quadrupled to generate light around 199 nm. The pulse energy of the frequency-quadrupled light is attenuated to be $<1 \mu\text{J}$.

For all the experiments described in this paper we employ two pulses that are referred to as pump and probe pulses. The temporal delay between the pump and probe pulses is set by a computer-controlled mechanical translation stage. Both beams are combined at a thin (1 mm) dichroic mirror and focused collinearly into a pulsed molecular beam of styrene, in the source region of a photoelectron imaging spectrometer, using a 250 mm fused silica lens. The cross-correlation of the various UV pump and probe pulses lies in the range 175-290 fs, measured by non-resonant ionisation of NO. The pulse energies of the pump and probe are attenuated to $<1 \mu\text{J}$ to ensure that no more than 20 electrons are generated by either the pump or probe alone, minimizing unwanted multiphoton ionisation and space-charge effects.

The photoelectron imaging spectrometer consists of two differentially pumped chambers separated by a 4 mm home-made skimmer. The source chamber houses the pulsed molecular beam (described below) and is pumped by a 2000 l/s maglev turbomolecular pump maintaining a base pressure of 8×10^{-8} mbar when the pulsed molecular beam is off and less than 2×10^{-7} mbar when the pulsed molecular beam is running. The detection chamber contains a velocity map imaging (VMI) spectrometer and a liquid nitrogen cold trap and is pumped by a 1000 l/s turbomolecular pump maintaining a background pressure of 9×10^{-8} mbar, which rises to 1×10^{-7} mbar when the molecular beam is running. The VMI spectrometer is based on the Eppink and Parker design³⁶ and consists of a set of three polished parallel field plates (repeller, extractor, ground) separated by 15 mm. The extractor voltage was approximately 0.7 of the repeller voltage, which was set to -1500 V or -2500 V for this work. The photoelectrons are accelerated through a 40 cm field-free region (surrounded by a layer of μ -metal shielding) and collected by a commercial imaging detector (Photek) comprising a pair of microchannel plates backed by a phosphor coated optical fibre bundle. A CCD camera detects the light transmitted through the fibre bundle and the images are collected on a computer. For each pump-probe delay, we collect pump only, probe only and pump + probe images, in sequence, for 20 seconds each. This is repeated several times (typically 30) for a total of 30 minutes for each time step. This helps reduce the effects of any long-term drift in power due to laser instabilities. The pump only and probe only signals are subtracted from the pump + probe signal to eliminate single colour contributions from the images. Photoelectron spectra are recovered from the raw images using the image inversion program pBasex.³⁷ The resolution of the photoelectron imaging detector is defined in terms of the resolution of the photoelectron velocity, Δv . Since the photoelectron

kinetic energy $\propto v^2$, the energy resolution is better for the lower kinetic energy photoelectrons. In this work, the resolution of the imaging detector as defined by the FWHM of the peaks observed in the (2+1) REMPI ionisation of xenon is ~ 90 meV at 1.46 eV and 165 meV at 2.76 eV.

Experiments were performed using a pulsed molecular beam of styrene created by passing helium at very low pressure (<100 mBar) through liquid styrene (Alfa Aesar 99.5%, stabilised with 4-tert-butyl-catechol) into an Even-Lavie pulsed valve. The valve was operated at 500 Hz (to minimize overheating) and held open for 10-13 μ s. The valve was mounted 135 mm from the entrance of a skimmer that separated the source and detector chambers, and the distance between the skimmer entrance and the interaction region of the VMI spectrometer was 210 mm.

4. Results

We present two experiments investigating the photoinduced dynamics of styrene following excitation to the two lowest excited singlet states. The first experiment tracks the population through S_2/S_1 and subsequently S_1/S_0 CIs, following excitation to S_2 with ~ 0.3 eV (2300 cm^{-1}) excess vibrational energy. The second experiment tracks the flow of population through an S_1/S_0 CI, following direct excitation to S_1 with ~ 0.6 eV (4600 cm^{-1}) excess vibrational energy. The dynamics are monitored using TRPES.

In figure 3, we present photoelectron spectra recorded following excitation of styrene with femtosecond laser light at 240 nm, corresponding to ~ 0.3 eV excess vibrational energy in S_2 , which after passing through an S_2/S_1 CI corresponds to ~ 0.9 eV excess vibrational energy in S_1 (see table 1). The probe wavelength is centered at 254 nm, providing a combined energy of 10.0 eV, *i.e.* above D_0 and D_1 (see table 1(b)). Figure 3(a) is the pump-probe spectrum recorded at $t = 0$ and shows that there are three overlapping bands. Using the ionisation correlations presented in table 2, and assuming that any excess vibrational energy is conserved, to a first approximation, during the ionisation process, bands around 1.2 eV, 0.5 eV and 0.1 eV are assigned to the S_2 - D_0 , S_1 - D_0 and S_1 - D_1 ionisation processes, respectively.

The dynamics occur over a wide range of timescales, so we split our presentation of the time-resolved photoelectron spectra into two parts: time-resolved photoelectron spectra from 0–60 ps are presented in figure 3(b) and time-resolved photoelectron spectra from -100–250 fs are presented in figure 3(c). The S_2 - D_0 band (1.2 eV) has a maximum around $t = 0$ and decays within a few hundred femtoseconds. In contrast, the S_1 - D_0 and S_1 - D_1 bands (0.5 eV and 0.1 eV) only reach their maxima once the S_2 -

D_0 band has decayed, and are then relatively long-lived, decaying on the timescale of tens of picoseconds. The integrated intensity of each band can be considered as an approximate measure of the population being projected from the excited state onto the ionisation continuum. Thus, a more quantitative picture of the dynamics can be obtained by plotting the time-dependence of the integrated intensity of each band individually. These integrated intensities are presented in figure 4. Again, we present the data in two parts: 0-50 ps integrated band intensities are presented in figure 4(a) and 0-500 fs integrated band intensities are presented in figure 4(b).

To deconvolute the dynamics of the molecule from the resolution of the instrument (sometimes called the instrument response function) we have performed a global fit to the temporal dynamics of each band. The fitted function is a convolution of the Gaussian laser pulse with an exponential decay and is plotted as a solid line in figures 4(a) and (b). The cross-correlation FWHM, which was determined from an independent measurement of the cross-correlation intensity by non-resonant ionisation of NO, was 203 ± 25 fs, but because of the uncertainty it was also included in the fit. The expression used to fit the data presented in figures 4(a) and (b) is:

$$f(t) = N \left(1 + \operatorname{erf} \left((t - t_0 - (\sigma^2 / \tau)) / (\sigma \sqrt{2}) \right) \right) \exp \left(-t / \tau + t_0 / \tau + \sigma^2 / (2\tau^2) \right), \quad (1)$$

where t is the pump-probe delay. The parameters were obtained by fitting all three decay curves together: time zero (t_0); $1/e$ lifetime (τ); the variance of the cross-correlation pulse width (σ^2). The full-width at half-maximum for the cross-correlation is related to the standard deviation, $\text{FWHM} = \sigma \sqrt{2 \ln 2}$, and is determined to be 235 fs from the fit. See supplementary information for the derivation of equation (1). The fitted value for t_0 lies within the estimated experimental error from our measured cross-correlation of the pump and probe pulses of ± 25 fs. All the fit parameters are presented in Table 3.

	ΔE (eV)	τ (fs)	σ (fs)	t_0 (fs)
$S_2 - D_0$	0.9 – 1.4	13	100	-23
$S_1 - D_0$ and $S_1 - D_1$	0 – 0.15, 0.15 – 0.8	18 820	100	-23

Table 3 The fit parameters for equation (1) obtained for the data presented in figures 4(a) and (b).

From the fit, the loss of population from S_2 occurs exponentially with a $1/e$ timescale of 13 fs and the concomitant gain in S_1 population occurs with the same $1/e$ timescale of 13 fs. The subsequent loss of population from S_1 occurs exponentially with a $1/e$ timescale of 19 ps. The fact that the loss of population from S_2 and the gain of population on S_1 occur on the same timescale is evidence that we are observing ultrafast (essentially instantaneous on the timescale of our experiment) decay through the S_2/S_1 CI. The upper limit for the $1/e$ decay of S_2 and rise of S_1 is approximately 45 fs (obtained from the fit). Despite the huge amount of excess vibrational energy in S_1 (~ 0.9 eV), the subsequent loss of population from S_1 is three orders of magnitude slower than decay through an S_2/S_1 CI, suggesting that there is effectively a barrier on the S_1 potential energy surface preventing ultrafast IC through an S_1/S_0 CI.

To investigate this further, we performed a new set of experiments in which we excited just below the onset of absorption to the S_2 state, populating S_1 with the maximum possible excess vibrational energy by direct excitation from S_0 (~ 0.6 eV). Initially, the probe wavelength was selected to be 240 nm so that we accessed the same region of the ionisation continuum as in the first set of experiments; however, the much larger cross-section for excitation to S_2 at 240 nm resulted in the photoelectron spectrum being dominated by the 240 nm pump + 254 nm probe process at short times, *i.e.* within the cross-correlation. This problem was solved by selecting a much shorter probe wavelength so that the unwanted bands resulting from S_2 excitation were well-separated from the bands arising from S_1 excitation.

In figure 5, we present photoelectron spectra recorded following excitation of styrene with femtosecond laser light at 254 nm, corresponding to ~ 0.6 eV excess vibrational energy in S_1 . The probe wavelength is centered at 199 nm, providing a combined energy of 11.1 eV, *i.e.* above D_0 , D_1 and D_2 (see table 1(b)). Figure 5(a) is the pump-probe spectrum recorded at $t = 0$ and there are three overlapping bands. As before, using the ionisation correlations presented in table 2, bands around 1.75 eV and 1.0 eV are assigned to the S_1 - D_0 and S_1 - D_1 ionisation processes, respectively. There is another band around 0.4 eV that is only present in the photoelectron spectrum during the time that the pump and probe pulses overlap temporally. This band is attributed to the unwanted S_3 - D_0 ionisation process and is a result of excitation to S_3 by the 199 nm probe pulse. Fortunately, the S_3 - D_0 band is reasonably well-separated, energetically, from the S_1 - D_0 and S_1 - D_1 bands.

The integrated intensities of the S_1 - D_0 and S_1 - D_1 bands are plotted as before as a function of pump-probe delay in figure 6. The decay rates of both the S_1 - D_0 and S_1 - D_1 bands are approximately the same at long times (*i.e.* beyond the cross-correlation time of the two laser pulses) and are also the same as the decay rate of the total integrated

electron count. The higher energy S_1 - D_0 band at 1.75 eV is well-separated from the S_3 - D_0 band at 0.4 eV. We can therefore fit this band to the same convolution of the instrument response function and an exponential decay described above. The experimentally determined cross-correlation was 287 ± 40 fs, with an error in t_0 of ± 100 fs. The S_1 - D_1 band has some overlap with the unwanted S_3 - D_0 band at short times when the pump and probe pulses overlap temporally. This results in an artificial peak in the integrated S_1 - D_1 band at short times. The effect of the S_3 component can be incorporated in the fit by the addition of another Gaussian that matches the laser cross-correlation width.

The S_1 - D_0 data presented in figure 6 is fit using equation (1), while the S_1 - D_1 data in figure 6 is fit using

$$f(t) = N \left(1 + \operatorname{erf} \left((t - t_0 - (\sigma^2 / \tau)) / (\sigma \sqrt{2}) \right) \right) \exp(-t / \tau + t_0 / \tau + \sigma^2 / (2\tau^2)) + N_2 \exp((-t - t_0)^2 / (\sigma^2 \sqrt{2})) \quad (2)$$

where all symbols have the same meaning as in equation (1). See supplementary information for a derivation of equation (2). The parameters were obtained by independently fitting the two decay curves. The parameters obtained from independent fits to both the S_1 - D_0 and S_1 - D_1 bands are presented in Table 4.

	ΔE (eV)	τ (fs)	σ (fs)	t_0 (fs)	N/N_2
$S_1 - D_0$	1.5 – 2.2	3 960	115	-71	
$S_1 - D_1$	0.8 – 1.5	3 220	115	-71	0.5/0.3

Table 4 The fit parameters obtained for equations (1) and (2) for the data presented in figure 6. The value for t_0 lies within our estimated experimental error of the absolute time-zero as measured via the cross-correlation of the pump and probe pulses of ± 100 fs.

From the fit, it is apparant that the loss of population from S_1 occurs exponentially with a $1/e$ timescale between 3.2 ps and 4 ps. Despite the fact that styrene has around ~ 0.6 eV excess vibrational energy in S_1 when excited directly from S_0 with light at 254 nm, compared to ~ 0.9 eV excess vibrational energy when populated indirectly *via*

the S_2/S_1 conical intersection following S_2 excitation with light at 240 nm, the decay from S_1 is of the order of five times faster.

5. Discussion

Experimentally, we find that S_1/S_0 radiationless decay in styrene is slower when the S_1 state is accessed *via* S_2 compared to direct access on S_1 , even when there is sufficient excess vibrational energy in both cases. Based on this result, we suggest the following outline mechanism.

- S_1 radiationless decay is barrier activated (picosecond timescale), *via* a conical intersection that does not occur along the initial geometry relaxation coordinate on this state.
- S_2 radiationless decay is barrierless (femtosecond timescale): the initial geometry relaxation leads directly to a conical intersection with S_1 .
- Geometry changes as a result of ultrafast decay from S_2 result in S_1 population that is ‘further’ from an S_1/S_0 crossing, which must be accessed indirectly along a different coordinate, leading to a difference in S_1 decay times.

We invoke conical intersections in our discussion rather than the more traditional Fermi’s Golden Rule type IC due to the time scales involved. The rate of Fermi’s Golden Rule type IC generally decreases with increasing vibrational energy,³⁸ and previous lifetime measurements of the S_1 state with low excess energy have shown lifetimes of the order of several tens of nanoseconds.^{15, 39-40} Therefore, it is extremely unlikely that the rate of S_1/S_0 IC would increase by three orders of magnitude with increasing excess energy, as we observe, without the appearance of a new IC mechanism.

The observations can be rationalised in terms of a model based on the excited state structures located in reference 15. In this CASSCF/4-31G study, CIs between S_1/S_0 were found at 5.41 eV and 6.03 eV above the S_0 minimum (these energies are certainly over-estimated, and cannot be compared directly with our highest experimental excitation energy which was 5.2 eV (240 nm)). The geometry of the higher-energy S_1/S_0 CI was determined to be similar to that of a twisted S_2/S_1 CI (where S_2 was a covalent excited state⁴¹), shown as the upper structure in figure 7: the only difference is that for this twisted S_1/S_0 CI, the ethylene carbon closest to the benzene ring is raised markedly out of plane. In contrast, the lower energy S_1/S_0 CI appears similar to the prefulvene geometry of the S_1/S_0 CI in benzene, *i.e.* the ethylene

and ethyl-benzene CC bond lengths are similar to those of the S_0 minimum, but the benzene ring has undergone a prefulvene-like out-of-plane distortion, shown as the lower structure in figure 7.

If the two CIs (S_2/S_1 and S_1/S_0) involved in the decay dynamics observed in our 240 nm S_2 pump experiments were similar geometrically, and located along the same reaction path starting at the Franck Condon geometry, one would expect that decay from S_2 to S_1 and subsequent decay from S_1 to S_0 would both be fast; indeed, faster than decay directly from S_1 alone. Because this is not the case in our 240 nm pump experiment, we deduce that in our experiments we observe decay *via* an S_1/S_0 CI having a very different geometry to that at which S_1 is accessed. Based on the outline mechanism above, one interpretation is that the initial decay from S_2 to S_1 is through a twisted CI and the subsequent decay from S_1 is through a very different prefulvene-like CI, as shown in figure 7. At present, we cannot say whether both decay sequences we have studied – from S_2 and separately from direct S_1 excitation – result in different rates for accessing a common region of an S_1/S_0 intersection seam such as the prefulvene one, or whether different crossings are involved in each case. This is of course only one interpretation based on the specific structures described in reference 15. Nonetheless, we expect any detailed interpretation to be consistent with this general model. To check our provisional interpretation would require further testing through accurate calculations of the excited state potential energy surfaces, including all relevant geometry changes and crossings.

6. Summary

TRPES has been used to study the ultrafast decay dynamics of styrene following excitation into the two lowest excited singlet states. Internal conversion between S_2 and S_1 and between S_1 and S_0 , have both been observed. The dynamics observed in S_1 are quite different depending on whether the state is populated directly by the absorption of a photon, or indirectly following IC from S_2 . Contrary to what might be expected, the more energetic molecule produced *via* IC from S_2 has a much longer S_1 lifetime than its less energetic counterpart. The observations have been explained in terms of geometries encountered by the molecule as it relaxes electronically back to the ground state, and the large geometry changes that would need to occur to allow IC to S_1 and subsequently to S_0 . Hopefully, these results will stimulate interest in using quantum molecular dynamics calculations to determine the decay path from the S_2/S_1 CI through the S_1/S_0 CI to S_0 , based on accurate potential energy surfaces for all of the excited states involved.

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Figure Captions

Figure 1

Schematic energy level diagram showing the four lowest, singlet states of styrene (S_0 , S_1 , S_2 , S_3) and the three lowest, doublet states ($D_{0,d1,d2}$) of the styrene cation. In the experiments described in this paper the pump pulse excites styrene with ~ 0.3 eV excess vibrational energy in S_2 (shown) or ~ 0.6 eV excess vibrational energy in S_1 (not shown). The timescale for S_2/S_1 IC and S_1/S_0 IC are marked Δt_1 and Δt_2 , respectively. There is an approximate propensity for the vibrational quantum number to be conserved during photoionisation; therefore, since $E_{\text{vib}}(S_1) < E_{\text{vib}}(S_2)$ we would expect the thresholds for ionisation to be in the same order, $I_{\text{threshold}}(S_1) < I_{\text{threshold}}(S_2)$ for a given doublet state of the cation. For a given probe energy, different electronic excited states of styrene will be projected onto different electronic states of the cation which will map onto different (but overlapping) portions of the photoionisation continuum (cartoon photoelectron spectrum on right hand side of figure).

Figure 2

Orbitals for the ground state wavefunctions of neutral styrene and the styrene cation used as reference orbitals for the expansion of the excited state wavefunctions calculated at the DFT HCTH/6-311+G* level. The horizontal dashed line separates occupied orbitals from unoccupied orbitals in the electronic ground states of the neutral and cation species.

Figure 3

Photoelectron spectra recorded following excitation of styrene with femtosecond laser light at 240 nm, corresponding to ~ 0.3 eV excess vibrational energy in S_2 , and a probe wavelength centered at 254 nm. The $t = 0$ photoelectron spectrum is presented in (a), highlighting bands around 1.2 eV (S_2 - D_0), 0.5 eV (S_1 - D_0) and 0.1 eV (S_1 - D_1). Time-resolved photoelectron spectra from 0-60 ps are presented in (b) and time-resolved photoelectron spectra from -100-250 fs are presented in (c).

Figure 4

Partial integrated photoelectron yields following excitation of styrene with femtosecond laser light at 240 nm, corresponding to ~ 0.3 eV excess vibrational energy in S_2 , for 0-50 ps (a) and 0-500 fs (b). Open triangles correspond to S_1 - D_1 ionisation, open circles correspond to S_1 - D_0 ionisation and filled circles correspond to S_2 - D_0 ionisation. The solid lines are global fits to the experimental data (see text and table 3).

Figure 5

Photoelectron spectra recorded following excitation of styrene with femtosecond laser light at 254 nm, corresponding to ~ 0.6 eV excess vibrational energy in S_1 , and a probe wavelength centered at 199 nm. The $t = 0$ photoelectron spectrum is presented in (a), highlighting bands around 1.75 eV (S_1 -D₀), 1.0 eV (S_1 -D₁) and 0.4 eV (S_3 -D₀). Time-resolved photoelectron spectra from -100-1200 fs are presented in (b).

Figure 6

Partial integrated photoelectron yields following excitation of styrene with femtosecond laser light at 254 nm, corresponding to ~ 0.6 eV excess vibrational energy in S_1 , for 0-6 ps (a) and 0-1400 fs (b). Open triangles correspond to S_1 -D₁ ionisation, open circles correspond to S_1 -D₀ ionisation. The filled circles in (a) correspond to the total integrated photoelectron yield. The data points and error bars are the average and ± 2 standard deviations of electron counts collected for 15000 laser shots. The solid lines are global fits to the experimental data (see text and table 4).

Figure 7

Cartoon illustrating geometries of the S_1/S_0 and S_2/S_1 CIs and the non-radiative decay routes following excitation of styrene with femtosecond laser light at 240 nm, corresponding to ~ 0.3 eV excess vibrational energy in S_2 and ~ 0.9 eV excess vibrational energy in S_1 after passing through S_2/S_1 CI.

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Supplementary information

S1. Time evolution of the excited state population

We assume Gaussian temporal profiles for the pump and probe pulses:

$$I(t) = \frac{A}{\sqrt{2\pi}\sigma} \exp\left(-\frac{1}{2} \frac{(t-t_0)^2}{\sigma^2}\right) \quad (1)$$

Neglecting any coherent effects, the population, $f(t)$, in any excited state, S_i , varies with time according to the formula :

$$\frac{df(t)}{dt} = \Sigma_{0i} I(t) - kf(t), \quad (2)$$

where Σ_{0i} is the excitation cross-section from the ground state to the electronically excited state S_i , and k is the total decay rate of the S_i state. This first order differential equation has a known solution:

$$f(t) = \exp(-kt) \int_{-\infty}^t \exp(kx) \Sigma_{0i} I(x) dx = \exp(-kt) \int_{-\infty}^t \exp(kx) \Sigma_{0i} \frac{A}{\sqrt{2\pi}\sigma} \exp\left(-\frac{1}{2} \frac{(x-t_0)^2}{\sigma^2}\right) dx$$

The convolution of the exponential and the Gaussian functions can be simplified and expressed in terms of the error function (see section S2), thus the time-evolution of the population in the excited state can be described by :

$$f(t) = \exp(-kt) \Sigma_{0i} \frac{A}{2} \exp\left(\frac{\sigma^2 k^2}{2} + kt_0\right) \left(1 + \operatorname{erf}\left(\frac{t-t_0-\sigma^2 k}{\sqrt{2}\sigma}\right)\right) \quad (3)$$

The decay rate, k , is related to the decay time, τ , by $k = 1/\tau$. By substituting for τ and setting $N = \Sigma_{0i} A/2$, we obtain equation (1) in the main paper:

$$f(t) = N \exp\left(\frac{\sigma^2}{2\tau^2} + \frac{t_0}{\tau} - \frac{t}{\tau}\right) \left(1 + \operatorname{erf}\left(\frac{t-t_0-\sigma^2}{\tau\sigma\sqrt{2}}\right)\right). \quad (4)$$

S2. Convolution of the exponential and Gauss functions

In order to solve the convolution integral,

$$\int_{-\infty}^t \exp(kx) \exp\left(-\frac{1}{2} \frac{(x-t_0)^2}{\sigma^2}\right) dx = \int_{-\infty}^t \exp\left(kx - \frac{1}{2} \frac{(x-t_0)^2}{\sigma^2}\right) dx, \quad (5)$$

the exponent in equation (5) has to be rearranged as shown below.

$$\begin{aligned} kx - \frac{1}{2} \frac{(x-t_0)^2}{\sigma^2} &= -\frac{1}{2} \frac{(x-t_0)^2}{\sigma^2} + k(x-t_0) - kt_0 = -\frac{(x-t_0)^2 - 2\sigma^2 k(x-t_0)}{2\sigma^2} + kt_0 = \\ &= -\frac{(x-t_0)^2 - 2\sigma^2 k(x-t_0) + \sigma^4 k^2 - \sigma^4 k^2}{2\sigma^2} + kt_0 = -\frac{(x-t_0-\sigma^2 k)^2}{2\sigma^2} + \frac{\sigma^2 k^2}{2} + kt_0 \end{aligned}$$

To simplify this expression, a new variable, y , and an upper integration limit, t' , is introduced as defined below:

$$y = \frac{x - t_0 - \sigma^2 k}{\sqrt{2}\sigma}, dx = \sqrt{2}\sigma dy, t' = \frac{t - t_0 - \sigma^2 k}{\sqrt{2}\sigma} \quad (6)$$

Combining the above mathematical transformations gives the resultant integral:

$$\int_{-\infty}^t \exp\left(kx - \frac{1}{2} \frac{(x - t_0)^2}{\sigma^2}\right) dx = \exp\left(\frac{\sigma^2 k^2}{2} + kt_0\right) \sqrt{2}\sigma \int_{-\infty}^{t'} \exp(-y^2) dy \quad (7)$$

Using the standard integral $\int_{-\infty}^0 \exp(-y^2) dy = \frac{\sqrt{\pi}}{2}$, expression (7) can now be derived

via the error function, $\int_0^t \exp(-y^2) dy = \frac{\sqrt{\pi}}{2} \text{erf}(t)$, as shown below :

$$\begin{aligned} \int_{-\infty}^t \exp(kx) \exp\left(-\frac{1}{2} \frac{(x - t_0)^2}{\sigma^2}\right) dx &= \exp\left(\frac{\sigma^2 k^2}{2} + kt_0\right) \sqrt{2}\sigma \int_{-\infty}^{t'} \exp(-y^2) dy \\ &= \exp\left(\frac{\sigma^2 k^2}{2} + kt_0\right) \sqrt{2}\sigma \left(\int_{-\infty}^0 \exp(-y^2) dy + \int_0^{t'} \exp(-y^2) dy \right) \\ &= \exp\left(\frac{\sigma^2 k^2}{2} + kt_0\right) \sigma \left(\sqrt{\frac{\pi}{2}} + \sqrt{\frac{\pi}{2}} \text{erf}(t') \right) \\ &= \exp\left(\frac{\sigma^2 k^2}{2} + kt_0\right) \sigma \sqrt{\frac{\pi}{2}} \left(1 + \text{erf}\left(\frac{t - t_0 - \sigma^2 k}{\sqrt{2}\sigma}\right) \right) \end{aligned}$$

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7