Dynamics of ultrafast internal conversion processes studied by
femtosecond time-delayed photoelectron spectroscopy

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ABSTRACT

We have studied the dynamics of ultrafast internal conversion processes using femtosecond time-resolved photoionization and photoelectron spectroscopy. In hexatriene, following femtosecond pulse excitation at 250 nm, we use time-delayed photoionization to observe the formation and decay of an intermediate species on the subpicosecond time scale. With time-resolved photoelectron spectroscopy, the rapid evolution of vibrational excitation in this intermediate is observed, as electronic energy is converted to vibrational energy in the molecule. The photodynamics of *cis* and *trans* isomers of hexatriene are compared and found to be surprisingly different on the 2-3 psec time scale. These results are important for understanding the fundamental photochemical processes in linear polyenes, which have served as models for the active chromophores of many biological photosystems.

Keywords: ultrafast, femtosecond, time resolved, dynamics, photoionization, photoelectron, hexatriene, polyene, internal conversion, relaxation

1. INTRODUCTION

With the advent of femtosecond lasers it has become possible to conceive of time-resolving ultrafast fundamental molecular processes which in the past were simply accepted as proceeding too rapidly to follow directly in time.¹ Previously, the study of fast examples of such processes as dissociation, isomerization, vibrational energy redistribution or internal conversion required the clever use of somewhat indirect methods such as frequency-resolved spectroscopy, chemical timing experiments, or in the case of dissociation, photofragment anisotropies. Our work is aimed at understanding the detailed mechanisms of these processes by observing, directly in time, the dynamics involved. The experiments described here demonstrate the applicability of femtosecond time-resolved photoionization and photoelectron spectroscopy to the investigation of ultrafast internal conversion.

The process of internal conversion plays an important role in the photochemistry of many organic molecules. Ultrafast internal conversion can convert electronic to vibrational excitation on a sub-100 fs time scale, producing vibrationally excited molecules at well-defined total energies that are far above barriers to isomerization or dissociation. Frequency-resolved spectroscopic studies can provide a great deal of information concerning the initially excited electronic state involved in internal conversion. However, for molecules that undergo internal conversion on a time scale much faster than spontaneous emission, very little can be learned about the relaxation processes using frequency-resolved techniques after the initial electronic dephasing time.

Time-resolved photoionization techniques are well-suited to the study of molecular dynamics of excited states in the gas phase. Photoionization detection is both sensitive and widely applicable, having the advantage of greatly relaxed selection rules compared to bound state spectroscopic methods. The first use of time-resolved photoionization was on a nanosecond time-scale, in a study of the triplet benzene lifetime.² It has subsequently been used for many measurements on nanosecond, picosecond and femtosecond time scales, with the first femtosecond study determining the lifetimes of Rydberg levels in benzene, toluene and their perdeuterated analogs.³ Recent femtosecond studies include the determination of a Rydberg state lifetime of NO,⁴ the photodissociation lifetime of ND₃,⁵ the observation of vibrational wavepacket motions in diatomics^{6,7,8} and photodissociation dynamics of, for example, OClO⁹ and iodobenzene.¹⁰

In most time-resolved photoionization studies ion yield alone is determined. However, measuring the kinetic energy of the photoelectron produced by the photoionization process can provide much additional information, since the internal

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energy of the ion is then determined. The ejection of a photoelectron is a fast, or 'vertical' process, so the neutral state being ionized is projected onto the energetically accessible vibrational levels of the ion which have the greatest Franck-Condon overlap. This characteristic offers the potential for following the molecular dynamics of an evolving system in great detail. Previous work demonstrating this capability includes picosecond time-resolved photoelectron spectroscopy which has been used to examine intramolecular vibrational-energy redistribution (IVR)¹¹ cluster dynamics,¹² and predissociation dynamics of Rydberg states of ammonia.¹³ Time-resolved variations of threshold, or zero electron kinetic energy (ZEKE), photoelectron techniques have also been applied on the picosecond scale^{14,15,16,17} to study IVR and have recently been extended to femtosecond time resolution to observe vibrational motions in small molecules.^{18,19}

The experiments presented here make use of both time-resolved photoionization as well as photoelectron spectroscopy in order to investigate the internal-conversion dynamics in a relatively large molecule, 1,3,5-hexatriene. While photoionization is broadly applicable, time-of-flight analysis of the photoelectron kinetic energy is particularly well-suited to studies where observing a wide range of ion vibrational energies is of interest. Time-of-flight energy analysis allows simultaneous collection of all electron energies, save those below a ~ 0.1 eV low energy cut-off, while simply requiring the output of a fixed-frequency laser. The latter feature is quite important, since it is difficult to scan the output of femtosecond lasers across a large energy range, while maintaining precise time delays, as would be required in a threshold photoelectron measurement of the same scope. Although the inherent energy resolution of time-of-flight analysis will never be the equal of techniques which detect threshold electrons, the ultimate energy resolution of photoelectron experiments involving femtosecond laser pulses is usually limited by the energy uncertainty (>100 cm⁻¹) due to the laser bandwidth.

Figure 1: Energy level diagram for both *cis*- and *trans*-hexatriene. Symmetry labels for the electronic states of *trans*-hexatriene are given first, with *cis*-hexatriene labels following in parentheses.

Hexatriene is one of the shortest of the general class of molecules known as polyenes, which possess alternating single and double bonds. It has been studied extensively, since polyene structures comprise the basis of the active chromophore in a variety of important biological systems, such as those involved in vision²⁰ and light harvesting.^{21,22} Hexatriene and larger polyenes can also be thought of as oligomers of polyacetylene,²³ a potentially important material that when doped or photoexcited exhibits high conductivity. Hexatriene possesses the same basic structure as the chromophore found in these various systems, and its relatively small size has made it an attractive model compound for theorists and experimentalists alike. Despite playing this role as a 'simple' analog for these more complicated systems, the fundamental photodynamics of hexatriene are not well understood. The strong $S_2 \leftarrow S_0$ transition near 250 nm has a linewidth greater than 150 cm⁻¹ even when hexatriene is jet-cooled.²⁴ One proposed explanation for this linewidth involves unresolved torsional excitation.^{25,26} However an absence of observed fluorescence following excitation of the S_2 state, as well as evidence from both resonance Raman studies^{27,28} and previous work in this laboratory,²⁹ indicates that the lifetime of the initially excited S_2 state is only ~ 40 fs for *trans*-hexatriene and ~ 20 fs for *cis*-hexatriene,³⁰ which accounts for at least most of the measured absorption linewidth. While the details of the nonradiative process responsible for the short lifetime of the S_2 state

have remained obscured, the possibility that its brevity stems from *cis-trans* (or *trans-cis*) isomerization seems unlikely given the results of resonance Raman studies^{27,28,31} which show that excitation to the S_2 state of each hexatriene isomer induces only little intensity in torsional modes. This is in contrast to the recently proposed behavior of biological systems incorporating polyenes, for which there is evidence that *cis-trans* isomerization is a vibrationally coherent process, occurring faster than the period of the torsional mode.²⁰ In hexatriene, it has been generally agreed that the most likely nonradiative process(es) from the S_2 state are internal conversion to either the lowest excited electronic state or the ground electronic state.^{24,27,28,29}

Somewhat surprisingly, the lowest excited state of *cis*-hexatriene was only recently experimentally located, confirming it to be the rather unusual 2^1A_1 state,^{32,33,34} in accord with longer polyenes. (In order to have consistent labels for analogous electronic states in both *cis*-hexatriene and *trans*-hexatriene, the generic designations of S_0 , S_1 , and S_2 are used for the ground $1^1A_g/1^1A_1$, first excited $2^1A_g/1^1A_1$, and second excited $1^1B_u/1^1B_1$ states of *trans/cis*-hexatriene respectively). The S_1 state has major contributions from double excitations,³⁵ which early one-electron calculations failed to properly model, originally resulting in the incorrect identification of the strongly optically allowed S_2 state as the lowest excited state. As Figure 1 illustrates, the S_1 state was found to lie 0.653 eV (~ 5275 cm⁻¹) below the S_2 state, at least in *cis*-hexatriene. The analogous state in *trans*-hexatriene is one-photon forbidden from the ground electronic state, thus far preventing experimental confirmation of its location; hence the ordering of the lowest excited states in *trans*-hexatriene is still a matter of some debate. However, the location of the S_1 state in *trans*-hexatriene is likely similar to that of *cis*-hexatriene, since the ionization potentials and $S_2 \leftarrow S_0$ excitation energies are nearly identical between the two isomers. The energy ordering of these two close-lying lowest excited states is an important factor in determining the energy relaxation processes involved in hexatriene, because internal conversion from the origin of the initially excited S_2 state to the S_1 state is of course only possible if the S_1 state lies at or below the energy of the S_2 state.

While no theoretical study of the time-resolved excited state dynamics of hexatriene has been made to this date, the dynamics of ultrafast internal conversion have received increasing attention in recent years. Domcke and coworkers have recently made many pertinent contributions in which they discuss excited state^{36,37} and internal conversion dynamics,^{38,39,40,41} as well as vibronically coupled systems.⁴² Of particular relevance to work presented here, some of these theoretical treatments have included calculations of time-resolved photoelectron spectra. Theoretical studies which specifically treat aspects of hexatriene have been concerned with, for example, modeling the $S_2 \leftarrow S_0$ absorption spectrum through the inclusion of unresolved low-frequency torsional mode excitation which adds to the apparent linewidth.^{25,26} The possibility of *cis-trans* isomerization beginning on the S_1 surface but producing ground state products is the subject of a CAS-SCF computational study reported by Olivucci et al.⁴³ Buck and coworkers⁴⁴ have undertaken calculations to investigate the photoisomerization of hexatriene and other small polyenes. Theoretical attempts to characterize the somewhat unusual S_1 state in polyenes, including hexatriene, have to a large degree focused on the vibronic coupling and electronic correlation involving the S_0 state,⁴⁵ which is proposed to explain the uncommon frequency increase, following $S_1 \leftarrow S_0$ excitation, of the symmetric C=C stretch in polyenes.

The specific goals of our experiments on hexatriene are to determine the time scales of the ultrafast internal conversion and vibrational energy redistribution processes that are involved in the molecular relaxation following S_2 excitation, and to follow directly in time the dynamics involved in the overall internal conversion process. Our approach to investigating ultrafast internal conversion dynamics incorporates both total ion yield experiments, which measure how the number of ions produced depends on the relative delay of the excitation and ionization pulses, and time-of-flight photoelectron spectroscopy, which for a given ionization delay provides a snapshot of the internal conversion dynamics. When these techniques are applied to hexatriene, we begin by exciting the origin of the S_2 electronic state with one 251 nm photon (see Figure 1). We then ionize the molecule using two photons from a second pulse (primarily at 377 nm, though some results will be presented from experiments which used a single 325 nm ionization photon) at some adjustable delay relative to the excitation time. By monitoring ion yield as a function of time delay, we observe the decay time of an excited state intermediate that is formed. At a given ionization delay we can project the intermediate(s) that are involved in the ongoing energy relaxation processes (internal conversion, vibrational energy redistribution) onto the ground electronic level of the ion and obtain time-of-flight kinetic energy measurements of the photoejected electrons. The resulting set of time-delayed photoelectron energy spectra provide an evolving picture of the dynamics which are occurring in the internal conversion and energy relaxation processes.

2. EXPERIMENTAL APPROACH

The laser system used in these experiments is based on a Ti:Sapphire femtosecond oscillator operating at 750 nm. Individual femtosecond pulses are first amplified to $\sim 40 \mu\text{J}$ at a 50 Hz repetition rate by double-passing through a dye amplifier stage using LDS 728 in ethanol as the gain medium. This stage is comprised of Bethune-type dye cells pumped with the doubled output of a Nd:YAG laser, as are the remainder of the dye amplifier stages used in our experiment. It is also isolated from both the oscillator and downstream amplifier cells by spatial filters. When a wavelength other than 377 nm is to be used for the ionization pulse, a portion of this initially amplified pulse is split off for use in continuum generation. This pulse first has positive linear chirp removed by prism-pair compression and is then tightly focused into a thin, rotating, optical flat to create a spectral continuum. From the continuum that is generated, a narrow wavelength region is selected using an interference filter having a 10 nm bandpass at twice the desired ionization wavelength. The chosen wavelength is then double-passed through a second Bethune cell dye amplifier, containing either LDS 698 in ethanol or DCM in methanol (for amplification near 700 nm or 650 nm, respectively). This amplified pulse is again temporally compressed using prism-pair compressors and frequency doubled using a 0.3 mm thick BBO crystal, producing a 10-15 μJ , ~ 150 fs pulse at the desired ionization wavelength.

The 377 nm ionization and 251 nm excitation pulses are formed by single-passing the portion of the initially amplified 750 nm light not used for continuum generation through a Bethune cell dye amplifier containing LDS 728 in ethanol. This pulse is amplified to 200 μJ , and following dispersion compensation in prism pulse compressors, pulse lengths of less than 100 fs are routinely achieved. Frequency doubling 754 nm pulses in an angle-tuned 0.5 mm BBO crystal produces light at 377 nm that is less than 150 fs in length. By then mixing the 754 nm and 377 nm pulses in an angle-tuned 0.3 mm BBO crystal a pulse near 251 nm is produced. The remainder of the 377 pulse can serve as the ionization pulse, if desired. The limited phase-matching bandwidth for the sum frequency generation process lengthens the 251 nm pulse to 200 fs as measured by cross correlation with the 377 nm pulse. The excitation and ionization lasers are combined in a Michelson arrangement with the relative delay between the excitation and ionization pulses varied under computer control with a 1 micron resolution motorized stage.

Experiments were performed in the differentially pumped ionization/detection region of a pulsed supersonic beam apparatus. Expansion conditions were chosen to avoid clustering: 800 Torr He was passed over hexatriene samples that were cooled to between -11 and -8 $^{\circ}\text{C}$ (hexatriene m.p. = -12 $^{\circ}\text{C}$). As Figure 2 shows in schematic form, the molecular beam is

Figure 2: A schematic illustrating the source, ionization and time-of-flight detection regions of the apparatus.

crossed at right angles by both the excitation and ionization pulses which are collinear. A 22 cm flight tube containing a removable stack of ion optics is orthogonal to both the molecular and laser beams, and has two concentric cylinders of shielding to minimize stray electric and magnetic fields. The ion optics allow the acceleration and time-of-flight mass detection of photoionized molecules using a microchannel plate detector. Ion yields are obtained by using standard boxcar techniques to process the ion signal while scanning the delay time in both directions across the full delay range to minimize any effects from laser power variations. With the ion optics removed from the flight tube, electrons ejected in the photoionization process can be energy analyzed by time-of-flight. In this study, signal was collected for either 50 000 or 100 000 laser shots at each delay time and processed using a digital oscilloscope controlled by a laboratory computer.

1,3,5-Hexatriene was purchased as a ~70:30 mixture of *trans*:*cis* isomers (Aldrich, Oakwood Products Inc.). To catalyze the conversion of the mixture towards the thermodynamically favored *trans*-hexatriene component, crystals of iodine were added and stirred under nitrogen for 48 hr., followed by vacuum distillation of the product.^{46,47} In a separate preparation, *cis*-hexatriene was isolated from the original mixture through the removal of the *trans*-hexatriene in a Diels-Alder reaction with excess maleic anhydride in the presence of 200 ppm hydroquinone under nitrogen, again followed by vacuum distillation of the product.⁴⁷ To avoid polymerization of the samples, they were kept near or below 0 °C and, perhaps more importantly, oxygen was excluded. The purity of the *cis*- and *trans*-hexatriene was ascertained through NMR analysis to be 99% and 93%, respectively, with the other isomer the only identifiable contaminant in each case.

3. RESULTS

Several recent results, some of which appear elsewhere,⁴⁸ are presented here to give an overview of our work-in-progress on hexatriene. The ion yield results which are shown first are from experiments similar to those previously undertaken in this laboratory to investigate the decay time of intermediates formed following photoexcitation of a commercially available mixture of hexatriene.²⁹ The differences in these more recent studies are that a molecular beam is used to jet-cool the sample prior to interrogation with femtosecond laser pulses and, more importantly, that pure isomers of hexatriene are isolated from the mixture and investigated separately, resulting in the determination of individual decay times for the intermediate formed in the case of each isomer. The remainder of the results stem from our recently developed capability to obtain time-delayed photoelectron spectra, which provide a more detailed picture of the dynamics of the relaxation processes.

A. Time-resolved ion yield experiments

Figure 3 shows the normalized photoion yield as a function of delay time between the peak intensity of the 251 nm excitation pulse and the peak intensity of the 377 nm ionization pulse, for each geometric isomer of hexatriene. Note that the combined temporal width of the two pulses means that even at a 'delay' of negative 100 fs, some fraction of the ionization pulse follows the early stages of the excitation pulse in time. Beyond 300 fs the two isomers have distinct decay times that are described well by exponential fits,

Figure 3: Ion yield as a function of the delay between the peak intensity of the ionization laser pulse and the peak intensity of the excitation laser pulse. Beginning at a delay of 300 fs, the ion signal due to *cis*-hexatriene and *trans*-hexatriene has been fit to an exponential decay. See text.

as shown in Figure 3, with time constants of 270 ± 50 fs for *trans*-hexatriene and 730 ± 50 fs for *cis*-hexatriene. These decay times are also found when other ionization wavelengths are used, indicating that they are characteristic of the molecules, independent of the wavelength used. As will be discussed, prior to 300 fs, the non-exponential nature of the decay curves primarily reflects the underlying dynamics of the internal conversion and energy relaxation processes that are occurring.

B. Time-delayed photoelectron spectroscopy experiments

In addition to the ion yield measurements, photoelectron spectra were obtained for both isomers at various ionization delays to map out the dynamics of the internal conversion and energy relaxation processes that are occurring during the time scale of our ion yield experiments. Figure 4 is a set of photoelectron spectra of *cis*-hexatriene obtained at various ionization delays, and plotted against the ion internal energy. Although this is perhaps a somewhat unconventional method of displaying photoelectron spectra, it allows rapid evaluation of the vibrational distribution in the ion. The spectra are split into two ionization delay ranges, with shorter delay photoelectron spectra, which are evolving rapidly, shown in the top frame. Longer delay photoelectron spectra, which are nearly constant, are shown in the bottom frame. One spectrum, taken at 200 fs ionization delay, is common to both frames to serve as a reference between the two frames. The spectra have been normalized to aid in the inspection of their relative shapes, however, the relative intensity of the spectra can be estimated by observing the relative height of the ion yield data, shown in Figure 3, at the corresponding delay time. The general trend of the photoelectron spectra is to proceed from a broad distribution of ion vibrational levels, including the very lowest vibrational levels, to a more narrow distribution peaked near 1.6 eV. As the partitioning of the spectra is intended to highlight, the shapes of the spectra become virtually identical after ~300 fs.

Figure 4: Photoelectron spectra taken of *cis*-hexatriene using various ionization delays, plotted as a function of the internal energy of the ion.

Figure 5: Photoelectron spectra taken of *trans*-hexatriene at various ionization delays, plotted as a function of the internal energy of the ion.

Figure 5 shows a set of photoelectron spectra taken of *trans*-hexatriene, over roughly the same ionization delay range, and at similar (although not identical) ionization delays as used in obtaining the photoelectron spectra of *cis*-hexatriene shown in Figure 4. As with Figure 4, the photoelectron yield is plotted against the hexatriene ion internal energy, and the relative scaling of the normalized spectra can be estimated by comparing the ion yield signal intensities presented in Figure 3, at the ionization delays used in the photoelectron experiment. To allow for easier inspection of the *trans*-hexatriene photoelectron spectra in Figure 5, they are separated into two ionization delay ranges. The early delay time *trans*-hexatriene spectra have greater intensity near the origin of the ion and also have reproducible, 'vibrational structure' in this region. The enhanced definition of vibrational structure may at least partially be a result of the greater signal-to-noise expected for this set of spectra, since the *trans*-hexatriene spectra were taken with 100 000 laser shots versus 50 000 laser shots for the *cis*-hexatriene. The ultimate trend of the *trans*-hexatriene photoelectron spectra is the same as observed in the *cis*-hexatriene, and they eventually proceed from a broad to a more narrow distribution again peaked well away from the origin of the ion.

When ionization is undertaken using more energetic ionization photons, one-photon ionization following excitation at 251 nm becomes possible. Figure 6 shows a spectrum taken with the excitation and ionization pulses overlapped in time (0 fs delay) using 325 nm as the ionization wavelength in an unfocused beam. The sum of the excitation and ionization photon energy is only 0.43 eV (3470 cm^{-1}) above the ionization potential (see Figure 1). This limits the vibrational levels that are accessible in the ion following one-photon ionization, and concomitantly limits the geometries of the intermediate from which ionization is possible to those having favorable Franck-Condon factors with the lowest vibrational levels of the

Figure 6: -- Photoelectron spectrum at zero ionization delay using one 325 nm photon to ionize *cis*-hexatriene following excitation at 251 nm, plotted as a function of ion internal energy. Note the expansion in scale along this axis from the previous two figures.

ion. A progression is formed in an anharmonic mode having $\sim 375\text{ cm}^{-1}$ spacing, but many other low vibrational levels appear to be populated, their individual peak widths contributing to an unresolvable distribution above 1000 cm^{-1} . Peaks corresponding to C=C or C-C symmetric stretch modes may be present near 1300 , 1500 and 1600 cm^{-1} , but are not prominent in the photoelectron spectrum even though there is sufficient resolution and photon energy to observe them.

4. DISCUSSION

Photoionization yield measurements under similar conditions were previously carried out in this laboratory on the commercially available mixture of *cis*- and *trans*-hexatriene isomers, confirming the short lifetime of the S_2 state, and observing an intermediate in the overall internal conversion process. In those experiments it was found that the internal conversion intermediate was effectively ionized using two photon ionization. The ion yield experiments presented here are further studies, using the individual *cis*- and *trans*-hexatriene isomers, of the time evolution of the molecule through this intermediate state. The wavelength of the ionization pulse in these experiments was chosen such that a single ionization photon has slightly too little energy to ionize the excited molecule and therefore all the signal observed is from absorption of two ionization photons by the excited molecules. The results in Figure 3 clearly show that the ionization signal following the initial excitation of the S_2 states of *trans*- and *cis*-hexatriene have distinctly different decay times, $270 \pm 50\text{ fs}$ for *trans*-hexatriene and $730 \pm 50\text{ fs}$ for *cis*-hexatriene. Since the ionization signal returns to the background level, the final product must not be ionizable. The measured decay times are both much longer than the known decay times ($< 50\text{ fs}$) of the initially excited S_2 states, so, as expected, they must correspond to an intermediate in the overall internal conversion process to the ground state. As in our previous studies the likely identity of the intermediate is the S_1 electronic state, and the measured decay times therefore correspond to $S_1 \rightarrow S_0$ internal conversion. Internal conversion to the ground electronic state, S_0 , produces a molecule with 4.9 eV of vibrational excitation, and thus very poor Franck-Condon factors with energetically accessible ion states. The ion yield as a function of time delay is therefore a measure of the time for which the excited neutral molecule has favorable Franck-Condon overlap with energetically accessible ion states.

Cis-trans isomerization is the characteristic reaction of linear polyenes, and is involved in many photochemical and photobiological processes. However, in 1,3,5-hexatriene, the distinct intermediate decay times in the ion yield measurements, demonstrate that rapid *cis-trans* isomerization must not occur while in the initially excited S_2 state or in the S_1 state. If *cis-trans* isomerization did occur completely on an excited state potential energy surface(s), then the product should remain ionizable, since both ions have essentially identical ionization potentials and both isomers of the hexatriene ion are known.

However, if a significant fraction of the molecules undergo isomerization in an excited state, then the decay times would become indistinguishable. It must be noted that *cis-trans* isomerization may be occurring during the $S_1 \rightarrow S_0$ internal conversion, resulting in the production of the other isomer on the ground electronic state. The lack of *cis-trans* isomerization during the interval in which the molecule is in the S_1 state is somewhat remarkable, given the presence of $>5000 \text{ cm}^{-1}$ of vibrational energy. Interconversion between the two geometric isomers might be expected based on calculations of a very low torsional barrier in the S_1 electronic state (the torsional coordinate comprises the reaction path in a *cis-trans* isomerization reaction), corresponding to a reduced bond order between the central carbons in this state. Indeed, a sharp decrease in fluorescence intensity relative to multiphoton ionization yield measurements is seen as the excitation is scanned farther than $\sim 100 \text{ cm}^{-1}$ above the S_1 origin in *cis*-hexatriene. This result has been interpreted to show that a nonradiative decay channel, proposed to be *cis-trans* isomerization, opens up near this energy.³⁴ Our time-resolved ion yield results are consistent with internal conversion between nearly planar S_2 and S_1 states where no large torsional excitation is produced. The lack of rapid *cis-trans* isomerization even for the short polyene hexatriene, where spectroscopy shows evidence of fast photodynamics, illustrates that the isolated polyene chromophore has quite different behavior than the substituted polyenes in biological systems, where *cis-trans* isomerization has been observed on a $<200 \text{ fs}$ time scale after photoexcitation.²⁰

An additional conclusion can be drawn based on the results of the two time-resolved ionization measurements. *Cis*-hexatriene appears to be more stable in the S_1 excited state than *trans*-hexatriene, at least when each has $\sim 5275 \text{ cm}^{-1}$ of vibrational excitation. As has been previously suggested,³⁴ the relative instability of the *trans*-hexatriene S_1 state may help to explain why efforts to locate it have failed under conditions where the S_1 state of *cis*-hexatriene has been observed.

The time-delayed photoelectron spectra of *cis*- and *trans*-hexatriene shown in Figure 4 and Figure 5 offer a more detailed picture of the energy relaxation process than is provided by the time-resolved ionization measurements alone. The general features of the spectra found in both Figure 4 and Figure 5 are consistent with the picture put forth to explain the time-resolved ion yield spectra. In both isomers of hexatriene, the positive ion and the S_2 state have very similar geometries. The S_1 state, on the other hand, is thought to have a significantly different geometry (different carbon-carbon bond lengths) from the S_2 state, and hence the ion ground state. At early delay times the photoelectron spectra have a broad distribution, in particular they extend all the way down to the vibrational origin of the ion (denoted 0 eV internal energy on these plots). The initial, short time delay, vibrational distribution in the ion reflects the fact that when the excitation and ionization pulses are overlapped, ionization of the S_2 state occurs. The origin of the S_2 state has favorable Franck-Condon overlap with the wavefunctions of low vibrational levels of the ion due to their similar geometry so photoionization of the S_2 state produces ions near 0 eV internal energy. However, even at the earliest times, some of the S_1 intermediate is present due to internal conversion of the S_2 state, since the S_2 state has a lifetime of only $\sim 20 \text{ fs}$ (*cis*-hexatriene) or $\sim 50 \text{ fs}$ (*trans*-hexatriene) which are short compared to the 200 fs excitation pulse. The geometries at which internal conversion proceeds are also governed principally by the Franck-Condon factors between the two states involved. Therefore, the S_1 state is initially at the geometry of the S_2 origin, distorted away from the S_1 equilibrium geometry. This ensures that directly following internal conversion, the vibrational modes that are excited in the S_1 state are modes which are active in the photoelectron spectrum, causing Franck-Condon intensity to be spread over a wide distribution of ion vibrational levels. The very broad ion vibrational distributions observed at delays less than 300 fs reflect the excitation of these specific Franck-Condon active modes in the evolving neutral molecule. In a short time, the vibrational excitation in the S_1 state is redistributed throughout the molecule, at least partially into modes that are less active in the photoelectron spectrum. The ion vibrational distribution narrows rapidly as the excitation of the active modes decreases. The fact that the spectrum ceases to evolve following 300 fs indicates that the intramolecular vibrational-energy redistribution (IVR) occurring on the S_1 state is complete on this time scale, at least to the extent that we are sensitive to. This is also consistent with the change in the shape of the ion yield spectra in the region of 300 fs. Once the IVR process is over, the ion yield decay reflects only the depopulation due to internal conversion of the S_1 state, while prior to the completion of IVR, the ion yield decay is faster, and non-exponential, reflecting both the declining Franck-Condon factors due to redistribution of the vibrational energy out of modes that have favorable Franck-Condon overlap with energetically accessible ion vibrational levels and the internal conversion of the S_1 state.

Although there are apparent differences between the rate of evolution of *cis*-hexatriene and *trans*-hexatriene photoelectron distributions shown in Figure 4 and Figure 5, closer inspection of the ionization delay times reveals that they are actually quite similar. At short delays the differences between the *cis*- and *trans*- spectra are due primarily to the substantially longer S_2 state lifetime in the *trans*-isomer, which produces a larger S_2 steady-state population during the excitation laser pulse. As a result, at early delays there is a much larger contribution from this state appearing near 0 eV in the *trans*-hexatriene ion vibrational energy spectra. At longer delays the primary difference is that for *trans*-hexatriene the IVR

rate and the intermediate state decay rate are comparable, so the molecule evolves through the S_1 state as fast as vibrational energy is redistributed. A final photoelectron spectra that is constant with time delay is achieved only after the S_1 population has substantially decayed.

It is important to reemphasize that the changes observed in the photoelectron spectra are due to changing Franck-Condon factors for ionization resulting from the evolution of the electronic and vibrational excitation in the neutral molecule. Therefore, the time for which the spectrum evolves primarily reflects the time scale for redistribution of energy from the initially excited vibrations of the S_1 state. However, since ionization of the excited neutral is a two photon process in these experiments, the detailed structure of the photoelectron spectrum may be influenced by resonances, such as Rydberg states, at the one-ionization photon level just below the ionization potential of the molecule. We are currently investigating the ionization wavelength dependence of the photoelectron spectra to assess the possible effects of resonances in the two-photon ionization, as well as developing one-photon ionization methods to detect the internal conversion intermediate. Keeping in mind the possible effects of resonance in the two photon ionization, an important observation about the photoelectron spectra may still be made. It is not surprising that ionization from the S_1 state results in a vibrational distribution in the ion that is peaked significantly away from zero, particularly when the S_1 state is formed with ~ 0.65 eV (~ 5240 cm^{-1}) of vibrational energy. The gradual threshold is characteristic of the photoelectron spectrum from a state of a neutral molecule with a substantially different geometry than the ion, and this is expected to be the case for the S_1 state of hexatriene.

The photoelectron spectrum shown in Figure 6, obtained using a single 325 nm photon to ionize *cis*-hexatriene following excitation to the S_2 state, is a first step toward using single photon ionization of the excited neutral molecule to study the internal conversion process. This spectrum is essentially a photoelectron spectrum of the S_2 state of *cis*-hexatriene, which lives for only 20 fs. A 375 cm^{-1} progression appears in the spectrum, peaked at the origin, that we assign to the totally symmetric in-plane bend of the carbon chain. While this frequency is lower than the 394 cm^{-1} observed for this mode in a resonance Raman investigation of the *cis*-hexatriene ion in a Freon glass matrix,⁴⁹ it is certainly possible that the matrix perturbs the frequency of this mode slightly, shifting it to higher frequency. The spectrum is much narrower than a He-I photoelectron spectrum of the neutral ground state (not shown) and does not show a progression in the ~ 1500 cm^{-1} C=C stretching vibration that is prominent in the He-I spectrum. This confirms that the originally excited S_2 state and the ion have quite similar geometries, much more similar than the ion and neutral ground state. The spectrum in Figure 6 also illustrates the nearly complete insensitivity of the one-photon ionization process to the S_1 state in this ionization wavelength range, shown by the lack of ion signal above 0.2 eV in Figure 6, as compared with Figure 4. This effect was studied in previous work, using ionization wavelengths as short as 310 nm, where one-photon ionization yield measurements showed no evidence for an intermediate.²⁹ The inability to follow the internal conversion process using one-photon ionization of the excited neutral molecule led to development of the two-photon ionization approach, used in the experiments reported here. Preliminary results from measurements using shorter ionization wavelengths, ~ 250 nm, indicate that relatively efficient, one-photon S_1 state ionization can be observed.

In conclusion, we have used the combination of femtosecond time-resolved photoionization and photoelectron spectroscopy to gain a much more detailed understanding than was previously possible of the fate of the initially excited state and the dynamics of the overall internal conversion undergone by the two geometric isomers of hexatriene. The dynamics of the process are quite different for the *cis* and *trans* isomers. They remain distinguishable after excitation for the 2-3 ps time scale of the experiments, indicating that there is no rapid interconversion between them on this time scale. The time-delayed photoelectron spectra observed for *cis*-hexatriene and *trans*-hexatriene are consistent with rapid internal conversion to the S_1 state and provide a vivid illustration of the speed of energy redistribution within this state. Detailed evaluation of the photoelectron spectra awaits comparison with ongoing experiments utilizing a single photon in the ionization step. Experiments are also planned to investigate 1,3-butadiene, whose excited state dynamics are even more poorly understood than those of hexatriene.

5. ACKNOWLEDGMENTS

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