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Towards quantum controlled initiation of explosives

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Abstract. As a first step toward understanding and controlling excited state dynamics in explosives, transient absorption spectra of Hexanitroazobenzene (HNAB) in acetone, Trinitroaniline (TNA) in acetone and Diaminoazoxyfurazan (DAAF) in dimethylsulfoxide (DMSO) were investigated in an ultrafast shaped pump/supercontinuum probe experiment for their dependence on single parameter control schemes. Two single parameter control methods, second order spectral phase (linear chirp) and the effect of pump energy on the amount of transmitted pump light were investigated. Novel transient absorption spectra were obtained for the three explosives. The spectral features found in the HNAB and TNA solutions had evidence of more complex control possibilities, while the spectral features of DAAF were dominated by intensity control.

Introduction

Direct optical initiation (DOI) of energetic materials using quantum control of localized energy deposition requires manipulation of how the deposited energy produces a critical size hot spot, which allows propagation of the reaction and thereby initiation. Looking at the material in solution allows for initial understanding of the energetic material characteristics. The hot spot characteristics needed for growth to initiation can then be studied using thin films of the energetic material. Achieving direct quantum controlled initiation (QCI) in thin film condensed phase systems requires optimally shaped ultrafast laser pulses to coherently guide the energy flow along the desired paths.

DOI detonators were developed to reduce unintentional initiation for an electrical source (ESD, lightning strike or any other source of electrical energy) but they lack the additional "lock and key" safety feature proposed by QCI. By obtaining active control over the dynamics of the quantum mechanical system of the energetic material we explore the possibility of directly initiating explosives with shaped laser pulses. Quantum controlled initiation experiments require 1) optimally shaped light pulses, 2) pulse shaping measurement, 3) feedback control algorithms and 4) feedback measurement methods.[1-3] The broad spectral distribution of a femtosecond laser pulse is specifically altered by a pulse shaper, thereby driving the molecular system towards a desired final product. A computer controls the pulse shaper and adaptive learning algorithm while utilizing direct feedback control to search for the electric field that controls the system. The unique time dependent electric field that leads to initiation will act as a "key" at minimal laser energy-initiation will only take place when the proper pulse shape is used.

In this paper we describe the necessary preliminary experiments performed to ensure that single parameter control schemes, such as linear

chirp and pump energy, do not dominate the control space necessary for QCI. In these experiments transient absorption spectra from 325-750 nm were obtained for three explosives of interest, hexanitroazobenzene (HNAB), trinitro-aniline (TNA) and diaminoazoyfurazan (DAAF). Dilute amounts of the explosive were dissolved in either acetone (HNAB and TNA) or DMSO-dimethylsulfoxide (DAAF) and compressed 400 nm femtosecond (~150 fs) pulses were utilized to obtain the transient absorption (TA) spectra. Linear chirp and pump energy, both single parameter control schemes, were employed to investigate the presence of simple control. The influence of simple intensity control mechanisms must be known before searching for more complex mechanisms.

Experimental Section

Complete details of the experiment are described in an earlier publication.[4] Briefly, a Ti:sapphire fs laser system, containing a Spectra Physics Tsunami oscillator and Spitfire amplifier, was employed in these experiments. The 1.1mJ, 1kHz, 800 nm laser light was separated into two beams, pump and probe. 98% of the light was directed towards a 0.25 mm thick BBO crystal, which doubled the light to 400 nm. The 400 nm pump pulse was further sent through and acoustic optical modulator (AOM) pulse shaper that consisted of a 4-f zero dispersion compressor.[5] The remaining 2% of 800 nm light, the probe beam, produced a white light supercontinuum (325-750 nm) by focusing a spatially selected (through an iris) and attenuated fraction of the 800 nm probe pulse into a constantly rastering 2 mm thick CaF_2 window. The white light was further separated into two beams, signal and reference, to account for pulse-to-pulse spectral variations. Pump and probe were overlapped in time and space in the sample and transient absorption spectra were acquired using two spectrometers (Ocean Optics USB4000, 200-850 nm, 2 nm resolution).

The High Explosive Science and Technology Group at Los Alamos National Laboratory synthesized all explosive samples used in these experiments. Sample solutions consisted of the following: a 1.38 mM solution of HNAB in acetone (Fisher Scientific- Optima grade), a 0.298 mM solution of TNA in acetone (Fisher Scientific-Optima grade), and a 0.437 mM solution of DAAF in DMSO (Aldrich- Acs grade). A 2mm liquid flow cell (Harrick DCL-M25) was utilized in a manner so that the sample was constantly exchanged and each laser shot interacted with a fresh volume of the solution being investigated. The single parameter spectral phase measurements were taken at 15, 60, and 15 ps time delays for HNAB, TNA, and DAAF respectively.

Transient grating frequency resolved optical gating (TG-FROG) was used to measure the 400 nm pulses to ensure starting pulses were compressed.

Results and Discussion

A compressed 3.5 μJ. ~150 fs, 400 nm pulse was employed to obtain the TA spectra, shown in Figure 1 below, for the HNAB, TNA, and DAAF solutions. The z-axes (ΔT/T) of the contour plots describe the change in transmitted probe light normalized to the transmission without the 400 nm pump laser. Each TA spectra showed interesting regions of either absorption or emission that were further explored for controllability.

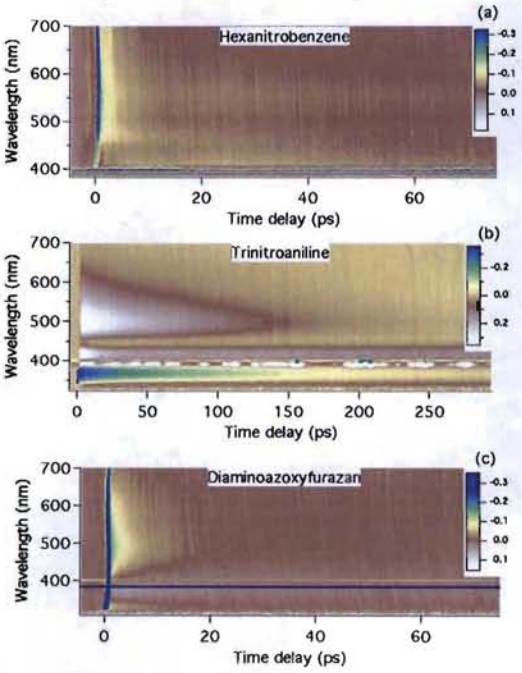

Fig. 1. Transient absorption spectra for HNAB (a), TNA (a), and DAAF (c). Spectra were obtained using a compressed 400 nm pump pulse and a supercontinuum (325-750) probe pulse. The ΔT/T z-axis color scales shows transient absorption for dark color and stimulated emission for white/light color.

HNAB

The transient absorption spectrum of HNAB shows two areas of interest, the absorptions around 460 and 550 nm. Both absorptions exhibit biexponentional temporal decay. The absorption at 550 nm has lifetimes of τ=17 and τ= 223 ps, while the 460 nm feature decays with τ=0.73 and τ=28.9ps lifetimes. The long lived 550 nm feature suggests it represents a final photochemical product and the 460 nm feature appears to be a decaying first excited state.

Each absorption region was tested with two single parameter control schemes, the effect of linear chirp and 400 nm pump energy dependence. Linear chirp implies a linear relationship of laser frequency with time, and is the simplest means of lowering the pulse intensity while maintaining the same energy and spectrum. Figure 2, below, shows the normalized effect of second order spectral phase on the signal intensity of the 550 and 460 nm absorptions. Each data point is normalized to the respective 550 or 460 nm signal intensity arising from a 400 nm compressed pulse. The linear chirp data at 550 nm is almost symmetric about the compressed, zero chirp pulse. The compressed, higher intensity, pulse gives the strongest normalized absorption signal while linear chirp decreases the signal by 20-40%. The response from linear chirp on the 460 nm feature is asymmetric about the compressed pulse and suggests the amount of absorption is dependent upon what frequency of light interacts with the solution first. Positively chirped pulses yield ~40% less normalized 460 nm absorption. Trends seen in the linear chirp data for 550 and 460 nm remains constant irrespective of 400 nm pulse energy (5, 3.5, 1.7, and 0.6μJ).

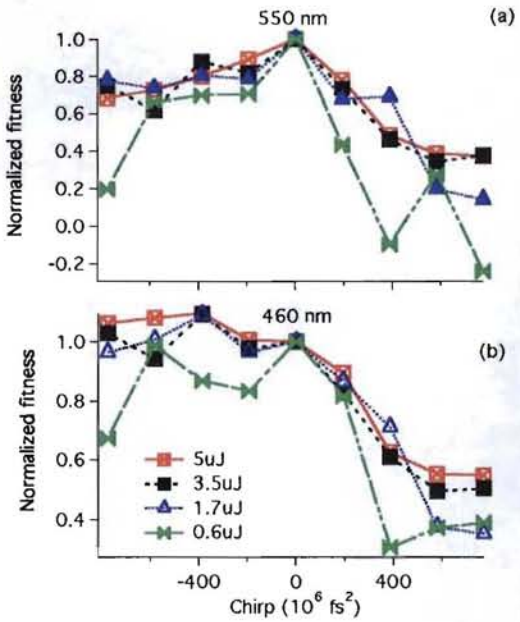

Fig. 2. HNAB linear chirp data for the two spectral regions of interest: 550 nm (a) and 460 nm (b). Data was taken for four energies 5 μJ (red- open box-solid line), 3.5 μJ (black- solid box-dashed line), 1.7 μJ (blue-open triangle-dotted line) and 0.6 μJ (green- bow tie-alternating dashed line).

Figure 3 below, shows the effect of linear chirp on the amount of 400 nm light transmitted through the sample cell as a function of energy. The 400 nm compressed pulse demonstrates the strongest effect of energy on percent transmission. An increase from 38 to 43% transmission is obtained by decreasing the pump energy from 5μJ to 0.6μJ. The positively and negatively chirped pulses were less effected by decreased energy with a 1-2% change in transmission, suggesting the system has some associated intensity control originating in multiphoton absorption.

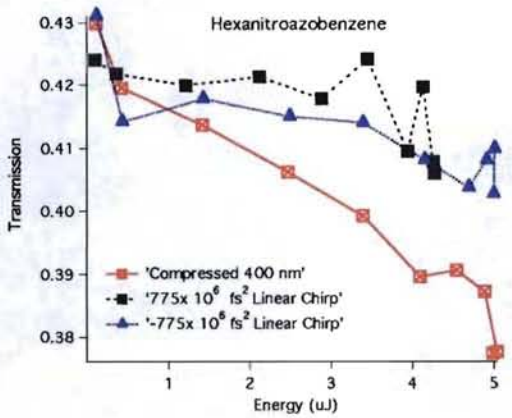

Fig. 3. The amount of light transmitted through HNAB sample cell for varying input energies and chirp values. Solid red box corresponds to compressed 400 nm results. Black solid box with dashed lines correspond to positive chirp response and blue triangles with dotted lines correspond to negative chirp response. Percent transmission increased with decreasing input energy and a larger response was obtained for the compressed pulse.

TNA

TNA's transient absorption spectrum has three strong areas of interest, two emission regions at 500 and 420 nm and an absorption region at 369 nm. The three features were fit to bi-exponentials. The emission at 420 nm is long lived with a life time of about 141 ps (τ= 8.6 ps, τ= 140.6 ps) and represents a ground state bleach. The 500 nm region has lifetimes of τ=12.4 ps and τ=101.6 ps and could represent either stimulated emission or a ground state bleach. The absorption at 369 nm has lifetimes of τ= 10.6 ps and τ=126.1 ps could represent an excited state.

The three notable regions were also tested for single parameter control. Figure 4 shows the normalized signals at 500 (a), 420 (b) and 369 nm (c) as a function of linear chirp for four energies (5,3.5, 1.7, and 0.6 μJ). The linear chirp data for the emission at 500 nm shows a similar effect for the various energy positively chirped pulses, namely signal intensity decreases with positive chirp. Conversely, the negatively chirped pulses show energy dependence. The higher energy more strongly negatively chirped pulses yield stronger 500 nm signal. Figure 4b shows a similar result to the 500 nm linear chirp data, absorption is dependent upon chirp in an asymmetric fashion. The absorption at 369 exhibits an intensity driven process for the higher energy pulses where chirp increases the signal by 10%. Lower energy pulses show less of an effect, corroborating intensity control.

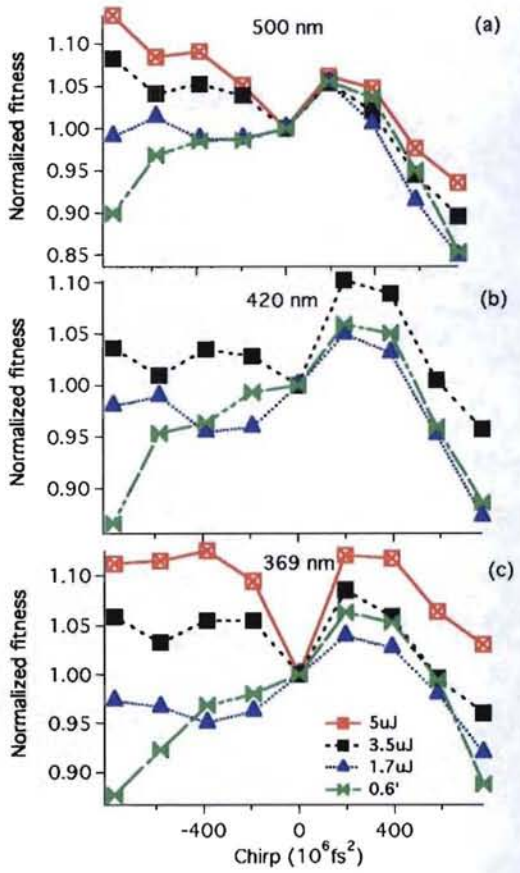

Fig. 4. TNA linear chirp data for the three spectral regions of interest: the emission data from 500 nm (a) and 420 nm (b) and the absorption data at 369 nm (c). Data was taken for four energies 5 μJ (red- open box-solid line), 3.5 μJ (black- solid box-dashed line), 1.7 μJ (blue-open triangle-dotted line) and 0.6 μJ (green- bow tie-alternating dashed line).

The percent transmission vs energy plot (Figure 5) demonstrates the increase in 400 nm light transmission for increasing energy. The negatively chirped pulse shows the largest increase in transmission with a gain from 11 to 19% for a ~6μJ pulse. The compressed and positively chirped pulses show similar trends where an increase from 11 to 17% transmission is seen for the highest energy pulses.

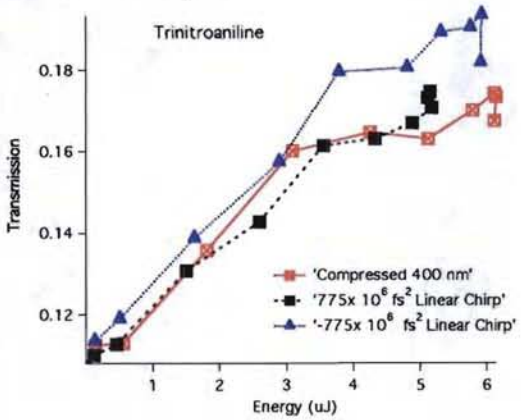

Fig. 5. The amount of light transmitted through the TNA sample cell for varying input energies and chirp values. Solid red box corresponds to compressed 400 nm results. Black solid box with dashed lines correspond to positive chirp response and blue triangles with dotted lines correspond to negative chirp response. Percent transmission decreased with decreasing input energy.

The long lived region of TNA at 420 nm is intriguing as it shows asymmetric character with respect to chirp. The asymmetric spectral dependence on the normalized output signal at 420 nm will be further investigated to determine if it can be utilized in a more complex active control scheme. The more symmetric character of the 369 nm linear chirp data, especially evident at the higher input energies, suggests single parameter intensity control is present.

DAAF

The transient absorption spectrum of a 0.44 mM solution of DAAF in DMSO shows absorption at 490 nm and ground state bleach at 383 nm. The short lifetime of the absorption (τ= 0.30 ps and τ=5.7 ps) suggests it is a decaying excited state. The 383 nm region was fit to a double exponential with lifetimes of τ=8.04 ps and τ=82.98 ps and represents a ground state bleach.

The linear chirp data show similar trends for the higher energy pump pulses, certain values of chirp increase the amount of absorption as well as ground state bleach (Figure 6). The curvature in both the 490 and 383 nm chirp data is indicative of an underlying photo-physical process where the inflection point in the yield suggests there are at least three excited states being populated[5]. Figure 7 shows the amount of control energy has on the amount of transmitted compressed 400 nm. It increases the transmission by about a factor of 2. The percent transmission of the strongly chirped pulses is less influenced by energy.

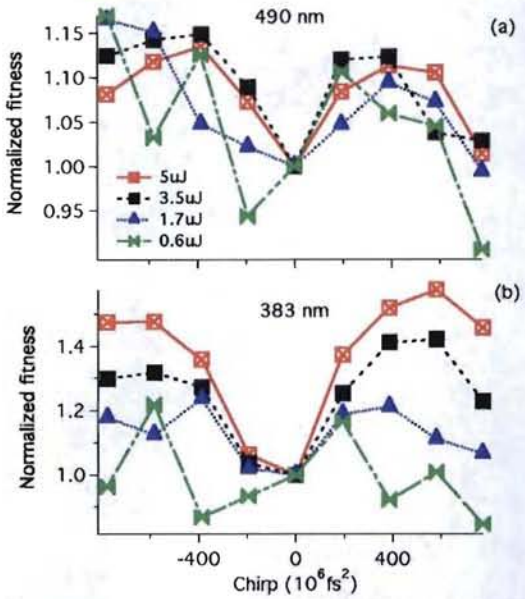

Fig. 6. DAAF linear chirp data for the two spectral regions of interest: absorption at 490 nm (a) and emission at 383 nm (b). Data was taken for four energies 5 μJ (red- open box-solid line), 3.5 μJ (black- solid box-dashed line), 1.7 μJ (blue-open triangle-dotted line) and 0.6 μJ (green- bow tie-alternating dashed line).

DAAF's transient absorption at 490 nm is controlled by intensity, as indicated by its symmetric response to linear chirp. Further

understanding of this data as well as the TNA and HNAB data requires theoretical calculations and specific assignments of the absorption and emission regions, which could be aided by information from linear spectroscopy.

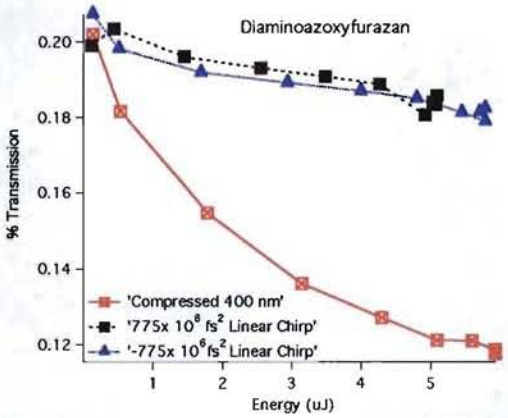

Fig. 7. The amount of light transmitted through the DAAF sample cell for varying input energies and chirp values. Solid red box corresponds to compressed 400 nm results. Black solid box with dashed lines correspond to positive chirp response and blue triangles with dotted lines correspond to negative chirp response. Percent transmission increased with decreasing input energy. The compressed 400 nm pulse exhibited about a 2 times increase in transmission with decreased input energy.

Conclusions

Necessary preliminary experiments have been preformed to determine if simple control parameters can drive the dynamics of dilute solutions of HNAB, TNA, and DAAF. Single parameter (intensity) control was obtained for both of the spectral features found in DAAF. Further investigations into the degree of intensity control are required to determine if more complex control is present. Conversely, HNAB and TNA have absorption and emission regions which did not have simple parameter control response, thereby suggesting the feasibility of implementing more complex control mechanisms potentially appropriate to act as a quantum key for initiation. The absorption at 460 nm in HNAB shows spectral dependence that needs to be further explored, while the linear chirp data from the emissions of 420 and 500 nm in TNA imply a spectral dependence on the multiphoton dynamics that may be exploitable for chemical control. More complex control schemes will be explored to drive the dynamics of all three explosives, but it should be noted that complete understanding of these systems require theoretical calculations and additional linear spectroscopy experiments.

Acknowledgments

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