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13. ABSTRACT (Maximum 200 words)

A facility for measuring time and wavelength resolved photo-induced absorption spectra based on step-scan fourier transfor techniques has been constructed and demonstrated. This facility is now doing measurements on the ms - ns timescales routinely and has been used to investigate photo-induced absorption in organic electron donor-acceptor systems in solution and thin film as well as crystalline inorganic systems. Proof of principle experiments have been performed with a streak camera to extend this method to the ps time scale.

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"Creation of a Multi-dimensional Spectroscopic Facility for the Characterization of Optical Limiters", F49620-98-1-0223, DAAG55-98-1-0255 Final Technical Report. Lee H. Spangler and Charles W. Spangler, Dept. of Chemistry, Montana State University, Bozeman MT. 59717

The purpose of this project was to assemble a facility capable of measuring photo-induced effects in potential optical limiting materials over a wide parameter space. In order to accomplish this efficiently, a facility capable of measuring both time and frequency resolved spectrum over a wide spectral range (UV -- IR) and over a wide range of temporal resolution was envisioned.

Introduction

One mechanism for optical limiting is reverse saturable absorption (RSA). In such systems an initial photon is absorbed creating a metastable, transient species in the material that has higher absorptivity than the original species. This transient species is then available to absorb additional photons thereby causing optical limiting. Figure 1 illustrates an energy level diagram for a reverse saturable absorber. For this mechanism to work for optical limiting, several constraints must be met: the initial absorption must have a lower absorptivity than that of the transient species; the absorption wavelength of the transient species and the original species must overlap; the transient species must form in a time short compared to the duration of the laser pulse. If any of these conditions are not met, the material will not limit efficiently. However, if some of these conditions are met it may be possible to engineer the material to fulfill the remaining conditions. Thus, simple performance characterization may eliminate a material with good potential.

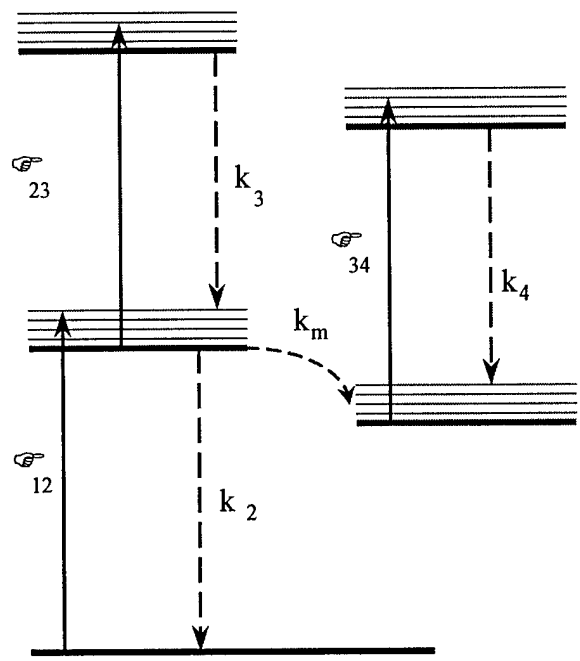

Figure 1. Energy level diagram for optical limiting via reverse saturable absorption. Absorption cross sections (σ) relaxation rates (k), and absorption frequencies all effect performance.

In order to produce good optical limiting materials it is desirable to have information concerning how efficiently the transient and species is formed, how quickly it is formed, it's relative absorptivity, and the absorption wavelengths of that transient species. Additionally, it is advantageous to obtain as much of this information as possible in a single experiment so that feedback to the synthetic effort can be provided on a timely basis. In order to accomplish this, time and frequency resolved photoinduced absorption measurements are necessary. Because there is interest in protecting both eyes and sensors, it is necessary to be able to measure of photoinduced effects in the visible as well as in the UV and IR. Because the overall material performance will depend on relative rates for different pathways within the mechanism, it is important to be able to measure photoinduced effects on a wide range of timescales.

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Approach and Methods

As stated in the introduction, our goal was to build a facility capable of measuring photoinduced absorption over a broad spectral range and temporal range with simultaneous time and frequency resolution. This required a method that could be adapted to different spectral regions yet still yield high information content in a relatively short time. This requirement for high information content necessitates a multiplexed method. One way of achieving multiplexing is to use a multi-element detector. However, this is expensive to implement over multiple spectral ranges and many array detectors would not have sufficient temporal resolution. Another approach is to multiplex in the time dimension by using a transit recorder or digital oscilloscope and a single element detector with a wavelength discrimination device such as a monochromator. We chose to use a method that provides multiplexing in both dimensions, wavelength and time. These methods are based on interferometric measurements and will be described below.

Fourier Transform Spectroscopy

Basics

Fourier transforms spectroscopy is a well-established method in the infrared (FT IR) but can also be applied to other spectral regions. In this method, wavelength discrimination is achieved by measuring how the light interferes with itself as opposed to using a dispersive element such as a grating or prism. This is accomplished by using a partially transparent element as a beamsplitter and entraining the light through two arms of an interferometer to two mirrors, then back on itself where it recombines at the beamsplitter. Moving one of the mirrors varies the path length on one arm and the resulting interference pattern is digitized at discrete points (usually determined by the zero crossing of the sine wave interference pattern of a reference HeNe laser). This interference pattern can then be mathematically transformed into a spectrum by use of a Fourier transform. Because all wavelengths of the broadband light are present in the interferometer at all times, this method is inherently multiplexed but only requires one detector element. As a result, the spectrum can be scanned it very rapidly and this method in works well for time dependent phenomena that occur on a millisecond to hour timescale. This standard method can be used to investigate photoinduced phenomena that occur, or relax, on a very long time scale. This can be accomplished simply by measuring the spectrum with the laser on versus the spectrum with the laser off. While this may seem like to long a timescale to be of interest for optical limiting, the length of a relaxation process is important to consider because many photoinduced absorption methods have fixed repetition rates that may be too fast for full sample recovery to the ground state. The end result is that a photoinduced absorption spectrum measured under these conditions would contain features that are due to a steady state population that a person while the sample is in the experiment and would not be indicative of the performance in the field. Thus, full understanding of the relaxation process and its consequences for a second pulse of a laser threat is important. This long-term relaxation can be difficult to measure by other methods for two reasons. Many dispersive systems that require scanning cannot scanned and appropriate wavelength range in that short a time. Many pulse methods have repetition rates that are too high and do not permit sample recovery.

Higher temporal resolution experiments can be performed with interferometers by operating them in step scan mode. If one considers that the interferogram is acquired by digitizing discrete points in the mirror travel, it becomes clear that the mirror could be moved in a step wise fashion rather than in the typical continuous fashion. This is not usually done in conventional instruments because stepping and stabilizing the position of the mirror is more difficult and then moving it continuously at a nearly constant velocity. However, when the mirror is moved in a step wise fashion, it allows for synchronization of modulated or pulsed experiments. Figure 2 illustrates how photoinduced spectrum can be acquired by use of a step scan interferometer, a method for amplitude modulating the pump beam and, phase sensitive detection such as a lock-in amplifier. Here, broadband light from a 50 watt, continuous tungsten lamp is passed through a sample and entrained through the interferometer. This sample is simultaneously pumped with a laser that is modulated either with a mechanical chopper or an AO modulator. A lock-in amplifier is amplifier is used to detect and amplify AC signal components that occur at the frequency of modulation. The resulting signal will be a difference between intensely at the detector with just the broadband light on versus both laser pump and broadband light. Thus, the signal can contain several photoinduced effects including photoinduced absorption, bleaching, and emission. This signal is detected at one mirror position by moving the mirror to a zero crossing of the reference HeNe laser, stabilizing the mirror, digitizing the data from the lock-in at that position, and then moving to the next mirror position. This is repeated for all necessary mirror positions to build up an interferogram, a process that takes 10 – 30 minutes, depending on the desired spectral resolution. And interferogram generated by this method is a difference interferogram for conditions about having the laser on versus the laser off. Since the Fourier transform that converts the interferogram to a spectrum is an integration, and because an integral of a difference is the same as a difference of two integrals, the difference interferogram can be directly Fourier transformed to yield to the difference spectrum. This method is an effective survey method and can be used to identify photoinduced absorption peaks but does not yield information about lifetimes, rates, or mechanisms. Sometime resolved information can be yielded from this method by varying the modulation rate of the laser.

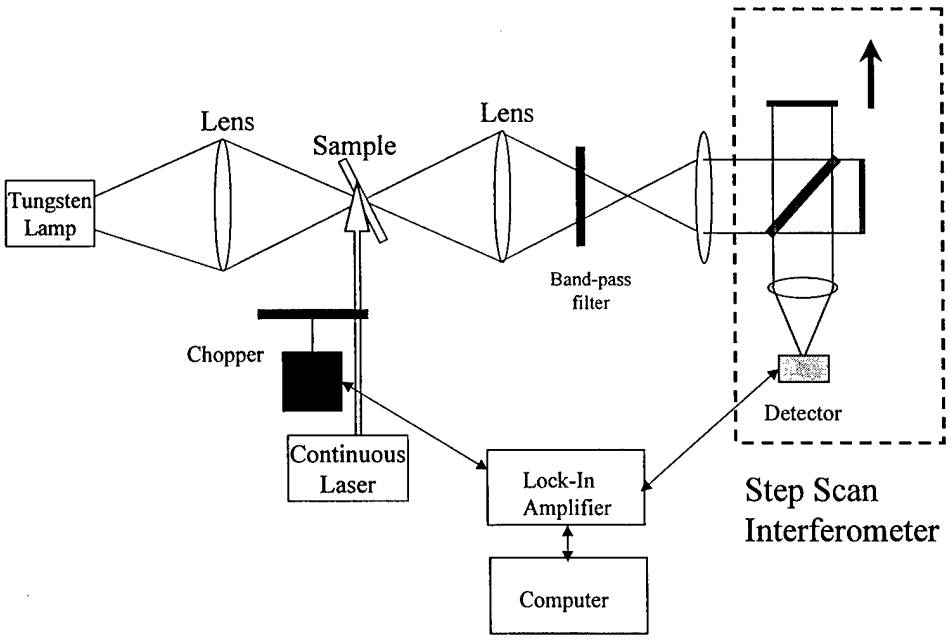

Figure 2. Step-scan modulated photoinduced absorption spectroscopy.

Step scan operation in an interferometer can also enable pulsed, time resolved experiments. Figure 3 illustrates this method for one of the simplest possible cases, a single frequency emission that decays exponentially. In this experiment, the mirror is stepped to a position, stabilized, and the laser is fired. The resulting transient signal is digitized using a transient recorder. The mirror is then stepped to a new position, the laser is fired again, and the transient signal is digitized once more. This process is repeated until the transient signal is acquired at each mirror position, and the resulting data set is a matrix of intensity as a function of both

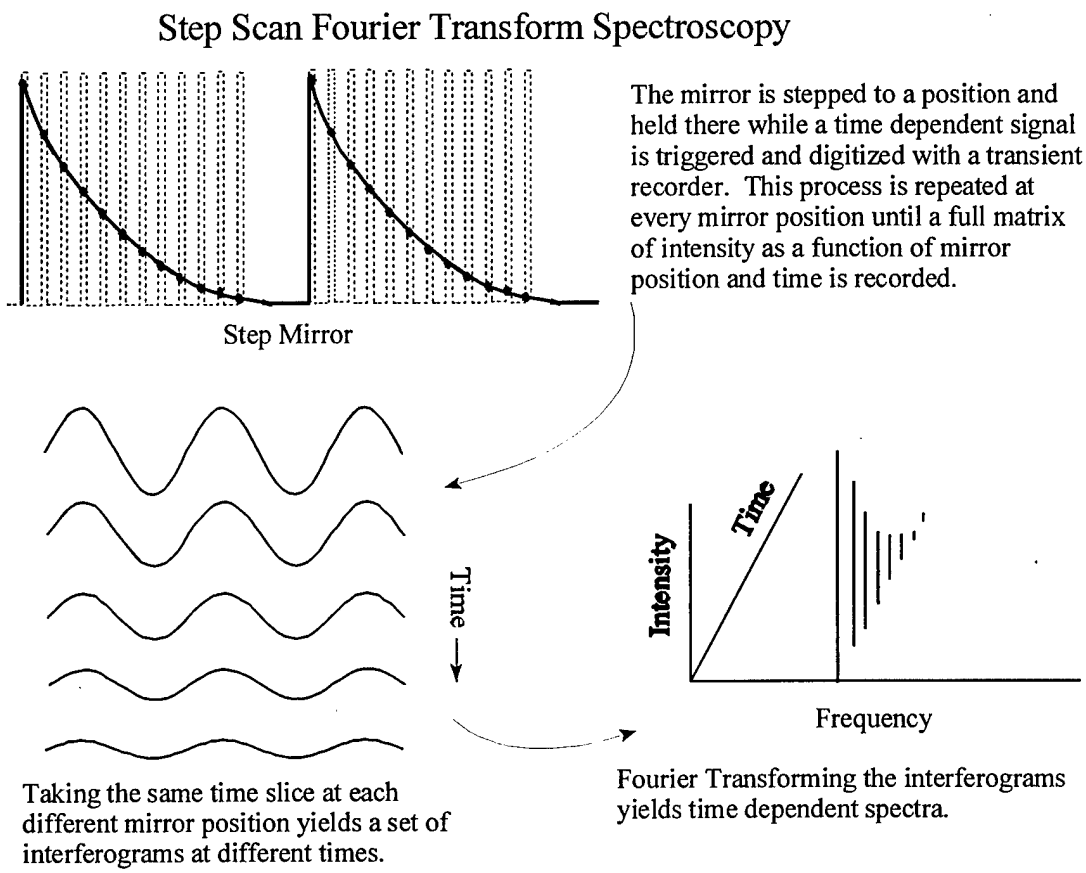

Figure 3. Step-scan, time and frequency resolved Fourier transform spectroscopy for the simple case of a single frequency exponentially decaying.

mirror position and time. If the first temporal data point is taken at each mirror position, an interferogram corresponding to this time is generated. That interferogram can be digitized to yield a spectrum at that time. Similarly, a spectrum at the fifth time slice can be generated by taking be the temporal data point at each mirror position and Fourier transforming that interferogram. This method can, of course, work for more complicated spectra and more complicated temporal behaviors. A fully time and frequency resolved photoinduced absorption spectrum can be acquired by this method by using a tungsten bulb and a pulsed pump laser. An advantage of this method is that the time and frequency resolution is generated using a single detector element so switching wavelength regions is a less costly. Additionally, because this method is multiplexed in the wavelength domain, a relatively low peak output broadband source can be used. It is possible to obtain reasonable signal to noise using a simple, continuous

tungsten lamp. By contrast, many flash photolysis experiments utilize a pulsed arc lamp, a source that is inherently less stable than continuous lamps and can lead to noise problems in the photoinduced absorption spectrum.

Facility Description

Equipment Acquired

Grants F49620-98-1-0223, AFOSR DURIP and DAAG55-98-1-0255, ARO DURIP were awarded for this project. The following equipment was obtained with these funds.

Bruker IFS 88 Step-Scan Fourier Transform Spectrometer.
This instrument is a Michelson interferometer capable of operating in both continuous and regular scan modes. Beamsplitters and detectors were also acquired with the system. The system also comes with software for data acquisition and manipulation. This instrument is key for performing time and frequency resolved, photoinduced absorption measurements

Hamamatsu Streak Camera.
This instrument allows direct, multichannel temporal resolution with up to 2 picosecond time resolution. This device can function in the 280 – 800 nm wavelength range and can function in several different triggering modes.

SpectraPhysics Regenerative Pulse Amplification System and Optical Parametric Amplifier.
This system enables the generation of 100 femtosecond or 2 picosecond pulses at a 1kHz repetition rate with high pulse energy and the ability to select wavelength. This system requires an oscillator which is described below.

Other Laser and Optics Available.
Several existing instruments, funded from other sources and projects, are also a part of this facility. We have a Coherent Ar ion laser pumped, ultrafast, modelocked Ti:Sapphire system that can be operated stand-alone, or as the oscillator for the pulse amplification system described above. A Coherent Infinity nanosecond pulsed Nd:YAG laser and a Lambda Physic OPO (which can be pumped by the Infinity) are also available and can provide high peak power, 5 ns duration pulses at repetition rates up to 100 Hz in the 270 – 2100 nm wavelength range. A second step-scan interferometer, a Bruker IFS 66, is also available. Beamsplitters and detectors are interchangeable between the IFS 66 and the IFS 88. Additionally, assorted oscilloscopes, electronics, lock-ins, power meters, and optics are available and were utilized in assembling the facility.

Thermal Analyst Modulated Differential Scanning Calorimeter
This system allows determination of polymer phase changes such as the glass transition temperature, and decomposition temperature. This is used for general characterization of polymers made from electron donating chromophores.

Waters System Gel Permeation Chromatography

This is for determination of polymer molecular weight distribution, number average, and weight average.

Results and Performance

We have set up the facility and have successfully demonstrated the ability to measure photoinduced absorption (PIA) effects in the region from 400 nm to 2000 nm using a continuous, 50 W tungsten bulb as the broadband source. PIA measurements to date have been performed primarily on charge transfer systems in solution and have not required ultra-high temporal resolution. We have performed PIA measurements on continuous to nanosecond timescales and have demonstrated the ultrafast capability on a model system. Additionally, we have performed modulated experiments and have begun investigations of charge transfer systems in polymer thin films. This information will be discussed in more detail below.

Continuous Scan PIA Experiments

These experiments are performed by scanning the spectrum under two different conditions, once with just the continuous, broadband light present, and a second time with both broadband and the continuous laser pump on. Spectra obtained this way are shown in Figure [redacted]. This method requires high stability in the spectral scan and drift or other systematic errors can greatly exceed the difference in the signal taken under the two different conditions. Because the FT method passes all wavelengths simultaneously and has throughput advantage (monochromators require a relatively narrow slit to provide reasonable resolution), spectra can be scanned in a very short time. By keeping the data acquisition time down to minutes or less, drift errors are minimized and accurate, direct measurements can be made. The data shown in Figure [redacted] are spectra for Mn^{4+} doped yttrium aluminum garnet (YAG), a robust, high damage threshold laser material at various times of laser exposure. The extremely broad transition is simply due to excited state absorption which has a small overlap with the ground state absorption at ~532 nm. This material does optically limit at 532 nm, but only causes a factor of 10 power reduction. Longer laser exposure results in a decrease in this absorption and the appearance of a new band at higher energy (lower wavelength). This new band requires minutes to fully relax after the laser is shut off indicating the formation of a metastable state. This is most likely due to ionization of the Mn ion. Similar behavior is seen in a different host (YALO) where EPR experiments indicate formation of a Mn^{3+} and Mn^{5+} from a pair of Mn^{4+} ions.

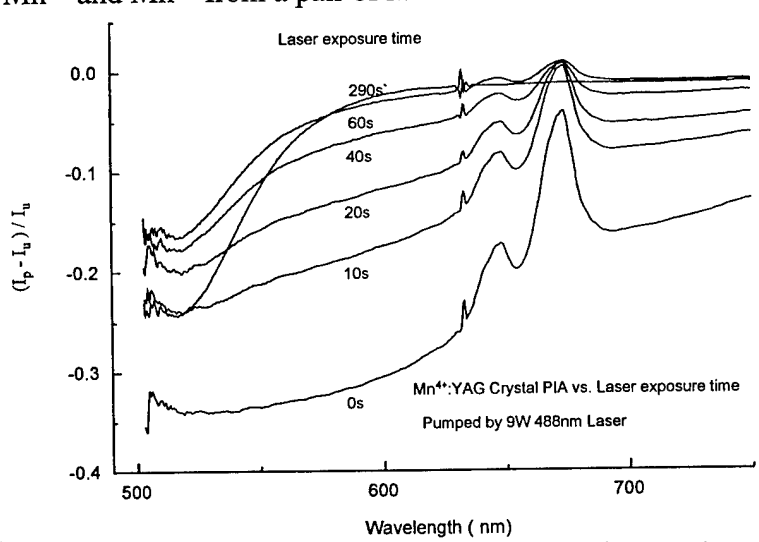

Figure 4 Continuous scan PIA spectrum of Mn:YAG. The spectrum is ΔT/T so photoinduced absorption features go downward. The positive going feature is emission

In certain cases we were also able to apply this method to organic donor – acceptor systems. A proprietary electron acceptor synthesized by Scientific Materials Corp. in collaboration with C. Spangler's group shows strong accepting characteristics when combined with the bis-(diphenylamino)diphenylpolyenes. A weak charge transfer peak attributable to the acceptor appears upon mixture of the donor and acceptor in solution. Excitation of the acceptor in solution by itself results in a moderately long lived PIA peak presumable due to triplet-triplet absorption. Excitation of the acceptor when it is in solution with the donor results in some quenching of this PIA transition and a new PIA peak at the same wavelength as the previous charge transfer transition indicating that the charge transfer can be photo-enhanced.

Modulated PIA Experiments

When sensitive measurements of difference spectra are required, phase sensitive detection and amplification are typically used. For measurement of PIA spectra, this requires modulation of the laser pump source and lock-in amplification. Acquisition of the modulated PIA spectrum with a laser pump, broadband lamp, a monochromator, and a lock-in amplifier is a commonly used technique, and one which is available in our laboratory. We can also perform modulated experiments with an interferometer in place of the monochromator. In this experiment, the demodulated signal from the lock-in is recorded at each mirror position while operating in step-scan mode. The result is a difference interferogram and Fourier transforming this interferogram directly yields a difference spectrum. An example difference spectra taken with an interferometer is shown. The sample is C_{60} plus bis-(diphenylamino) diphenyltriene at 5×10^{-4} concentration each in orthodichlorobenzene. (ODCB). The C_{60} was photoexcited at 514 nm with an Ar^+ laser which was modulated with a mechanical chopper at ~150 Hz. Both the interferometric and dispersive methods yield good spectra, however, data acquisition with the interferometer is faster, only requiring ~15min. per spectrum. A current *disadvantage* of the interferometer technique is that data can only be acquired on one side of the HeNe reference wavelength at a time (i.e. a single spectrum cannot cross the HeNe). This is a limitation with all currently available commercial instruments and is non-trivial to change. Monochromators due suffer an analogous problem in that spectra cannot be acquired in regions where two dispersion orders overlap without the use of filters. Because the method essentially integrates over 180 degrees of phase difference, it preferentially amplifies longer-

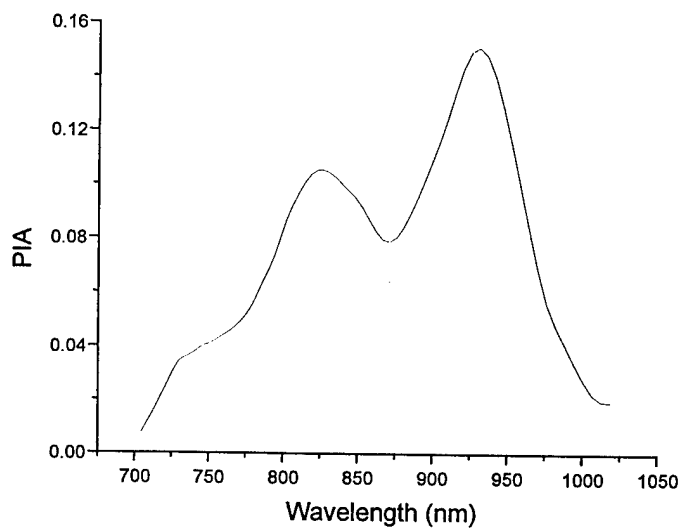

Figure 5. Modulated PIA spectrum of C_{60} plus bis-(diphenylamino) diphenyltriene at 5×10^{-4} M each in ODCB. Pumped by100mW of unfocused 514.5nm. The laser was modulated with a mechanical chopper and the spectrum was acquired with a step-scan interferometer and lock-in amplifier.

lived, photo-generated species, which are usually the charge-transfer species. As a result, it is a good method for screening materials to see if charge transfer is occurring, but yields little information about mechanism because shorter-lived intermediates may not be observed. The best mechanistic information comes from observing the formation and decay rates of various species and the modulated method can only provide crude temporal information (by varying the modulation frequency)

Pulsed PIA Experiments

This method provides time and frequency resolved data on time scales from .3 ns to milliseconds and we are actively pushing the method to the ultrafast as described in the next section below. In these experiments we pass broadband light from through the sample, and pump quasi co-linearly with a 3-5 ns laser pulse from a Nd:YAG or an OPO or dye laser pumped by an Nd:YAG. Unlike many flash photolysis methods, the broadband source is continuous (rather than pulsed) providing a more stable source and the method is resolved in both dimensions (time and wavelength) instead of resolved in one and sampled in the other. Figure [redacted] shows the time and frequency resolved PIA spectrum of Mn:YAG obtained by this method. As the data illustrates, large spectral and temporal ranges can be covered in a single experiment. This data was acquired with 100 cm^{-1} spectral resolution, 50 ns temporal resolution, a 10,000 cm^{-1} spectral

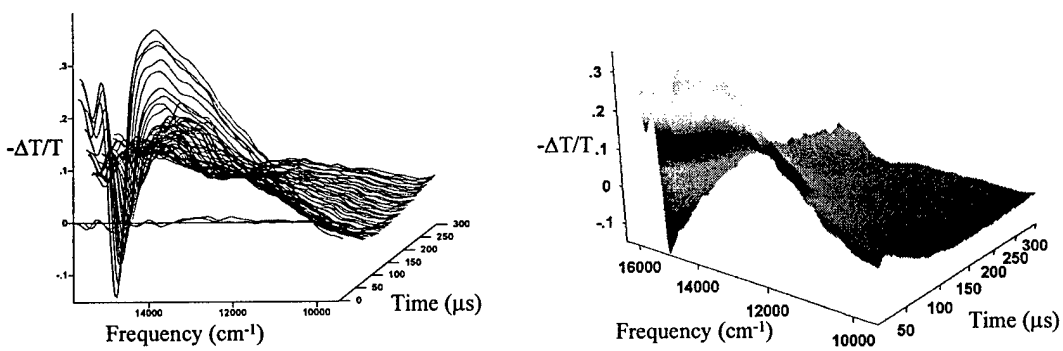

Figure 6 Two views of the pulsed, step-scan time and frequency resolved PIA spectrum of Mn:YAG after pumping with a 5 ns 532 nm laser pulse. The spectrum is - ΔT/T so photoinduced absorption features go *upward*, opposite of Figure 4. The negative going feature is emission.

range and a 20 μs temporal range. The data is comprised of 400 spectra at different times and took only 20 minutes to acquire, a rate of six seconds per spectrum. Spectral resolutions up to 1 cm^{-1} are possible but are not typically necessary for optical limiter studies because the materials have broad bandwidths. Higher resolution increases data acquisition time in a linear fashion so resolutions to ~10 cm^{-1} remain practical. Temporal resolutions from 0.35 ns to several milliseconds are available via this method.

Figure 7 shows the time and frequency resolved PIA spectra of C_{60} and of a C_{60} plus plus bis-(diphenylamino) diphenyltriene mixture in ODCB solution. Both solutions were pumped at 532 nm which excites the C_{60}. For C_{60} alone, the familiar triplet-triplet PIA absorption band is observed at 13,500 cm^{-1}. When the bis-(diphenylamino) diphenyltriene electron donor is added to the solution, the C_{60} triplet decays faster (Figure 7, bottom) and new transitions, primarily at

lower energies, rise at the expense of the C_{60} triplet. These new transitions are due to charge transfer species and are the cation of the polyene as confirmed by chemical oxidation. At early times, an isobestic point between the C_{60} triplet and the polaron (polyene cation) is observed indicating that both species are dependent on the C_{60} population. This, and the complimentary nature of the C_{60} decay and the polaron rise, verify that the charge transfer occurs out of the C_{60} triplet.

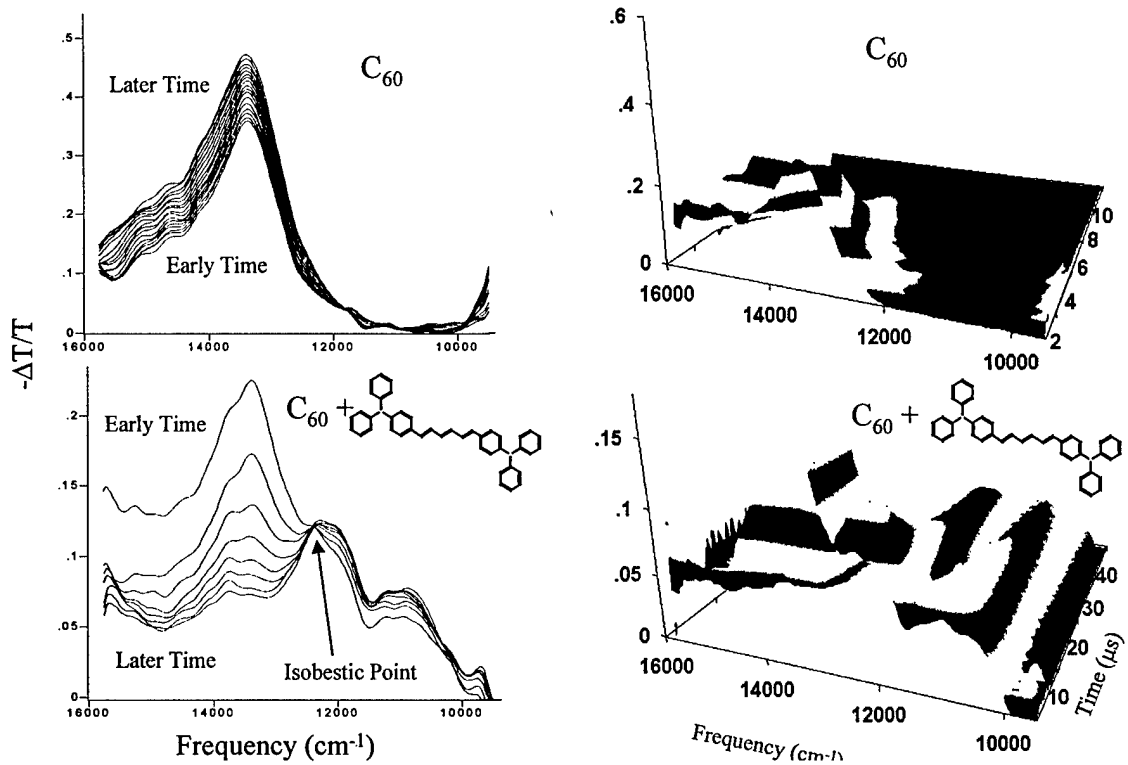

Figure 7. Two views of the C_{60} (top) and C_{60} + bis-(diphenylamino) diphenyltriene time and frequency resolved PIA spectra. The samples were pumped at 532 nm with < 1mJ / pulse. Note that the C_{60} triplet-triplet emission is rising (top left) when in solution by itself. This emission is quenched by the electron donor (bottom left). The three peaks seen at later times for the combination solution are due to the polyene polaron. The isobestic point (bottom left) indicates that the polaron population grows at the expense of the C_{60} triplet.

Ultrafast

We are investigating two methods of acquiring time and frequency resolved data on the ps timescale, both of which are based on use of a streak camera. A streak camera is basically a time to space converter comprised of a streak tube and imaging system. Photons entering the streak tube strike a photocathode and yield photoelectrons. These photoelectrons traverse a vacuum tube where they pass through a sweep electrode with a very fast voltage ramp. The effect of the ramp is to sweep early arriving electrons (generated by early arriving photons) upward, and later arriving electrons (from later photons) downward. These electrons enter a microchannel plate which provides ~10^4 gain. The electrons then hit a scintillator and the photons generated by that

device are then imaged on a CCD. The system is essentially an image intensified CCD array detector with a front end (sweep electrode) that converts the vertical spatial axis to a time axis.

The specifics of how the voltage on the sweep electrode is ramped are dependent on desired temporal resolution, temporal range per exposure, and the characteristics of the laser system used in the experiment. For the experiments proposed here, relatively high peak powers are necessary, and exceed what is available by appropriate frequency conversion commercially available, mode-locked Ti:Sapphire laser systems. Additionally, the typical sample relaxation times are not compatible with the 76 MHz repetition rate of our laser which provides 10 – 13 ns between pulses. For these reasons, pulse amplification in a regenerative amplifier is necessary. This provides high peak powers which enables frequency conversion via an optical parametric amplifier (and subsequent harmonic generation or sum frequency mixing) to the appropriate wavelength. It also reduces the repetition rate to 1 kHz to allow energy build-up in the amplifier rod. We have the mode-locked Ti:Sapphire laser (Coherent Mira pumped by a Coherent Sabre Ar^+), regenerative pulse amplification system (Spectra Physics Spitfire pumped by a SP Merlin) and OPA (SP) with all the frequency conversion packages including sum-frequency generation, which provides the highest peak power in the wavelength of interest. This system can be operated at nominal pulse durations of 150 fs or 2 ps and repetition rates below 1 kHz can be selected if necessary to permit full relaxation of the sample.

While the reduced repetition rate is convenient for sample relaxation, it does potentially effect streak camera operation as alluded to above. The way to obtain the highest temporal resolution is to synchronously scan the sweep electrode (synchroscan mode) at the frequency of the laser system with a sinusoidal voltage function. This works well at high repetition rates such as the 76 MHz of the mode-locked system and is typically not offered at lower rates. A second electrode sweeps the electrons horizontally, off the image intensifier to prevent overwriting the data on the return sweep. The result is an oval shape sweep pattern (the simplest Lissajous figure), half of which is "off screen". This operating mode can provide up to 2 ps temporal resolution in a Hamamatsu C5860 streak camera, but at a 76 MHz sweep frequency. A second sweep mode provides a linear voltage ramp with each trigger (single sweep mode). This method suffers from larger jitter and limits resolution to ~10 ps, but is typically used with ultrafast pulse amplification systems. We have both operating capabilities and an additional option as well. Our system was delivered with a second horizontal sweep unit which sweeps the entire oval Lissajous pattern off screen, then sweeps it back on (Figure 8) at a 1 kHz repetition rate, allowing us to operate in the high resolution synchroscan mode but at the lower

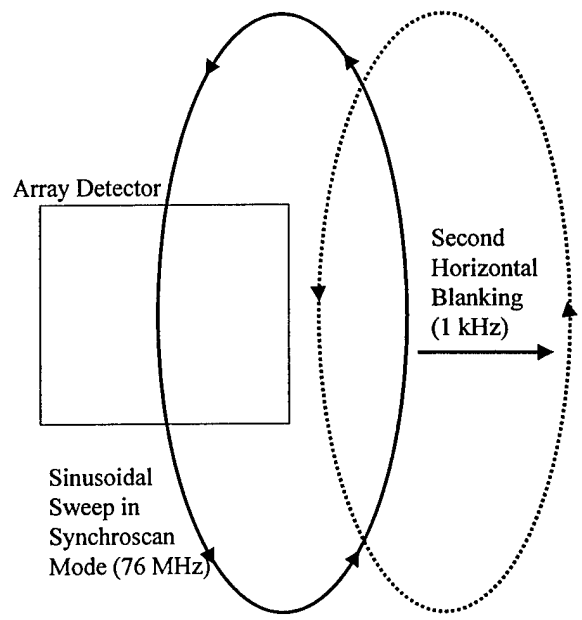

Figure 8. Synchronous sweep mode of the electron stream in a streak camera.

1kHz repetition rate. ***Ours is the first and only system delivered in the US with this special synchroscan blanking capability that permits the higher temporal resolution in combination with the 1 kHz repetition rate of regeneratively amplified systems.*** This capability is especially important for PIA measurements because it will allow use of a continuous source for the broadband light. Without the second blanking unit, the PIA effect would be detected at 1kHz but the broadband would be recorded at 76 MHz and would completely mask the PIA effect.

To this point, we have discussed the excitation source, the multichannel, temporally resolved detection, and the synchronization between the two. A method of obtaining spectral resolution is also needed. This is typically accomplished by placing a monochromator in front of the streak camera. The intensified CCD inside the camera is a 2-D array detector. The sweep electrode converts the vertical spatial direction to time. Placing the monochromator in front of the camera converts the horizontal spatial axis to wavelength. Because there are multiple detector elements in both dimensions, the system is multiplexed in both dimensions and each of the detector elements has significant gain. However, there is a fixed number of pixels in the detector so there is an inherent trade-off between resolution and range covered in both the spectral and temporal dimensions. The active area on the photocathode of the streak camera is ~ 5mm. With our Acton 0.3 m imaging monochromator and a 150 groove/mm grating, the spectral range covered in a single image is ~120 nm. Use of an 80 μm input slit will provide 2 nm spectral resolution. At 22 ps temporal resolution in the special synchroscan mode, the full temporal range covered will be ~2.2 ns. This means that the large spectral-temporal regions of interest can be captured with relatively high resolution (2 nm and 22 ps) *in each laser shot*. Multiple shots can be averaged at a 1 kHz rate to yield better signal / noise. Higher temporal resolution, up to 2 ps, can be obtained but at the expense of spectral range per exposure (150 ps at this resolution). We have extremely accurate electronic delays that will allow us to combine streak camera images to cover larger temporal ranges at higher resolution. Similarly, images can be acquired at different monochromator settings to cover a larger spectral range.

While this method has been successfully used by others to yield good quality time and frequency resolved data, it does have limitations. The small active area of the streak camera photocathode greatly reduces throughput in the system because it forces the use of lower dispersion gratings linked with small slit sizes to achieve reasonable combinations of resolution and spectral range. Interferometers, used to perform Fourier transform (FT) spectroscopy, typically have higher throughput and no trade-off between resolution and spectral range.

We have interfaced the streak camera with the step scan interferometer to extend the FT based time and frequency resolved spectroscopy to the picosecond time scale. In this experiment, the interferometer is operated in step-scan mode, and a streak camera image is recorded at each mirror position (Figure 9).

The vertical dimension of the image still contains temporal information, but the spectral information is contained across the images at multiple mirror positions. The horizontal dimension of the image is still spatial. Thus, a single pixel across multiple mirror positions contains one interferogram and Fourier transforming it will yield a simple spectrum. Fourier transforming a column of pixels across all mirror positions will yield a time and frequency resolved spectrum. The horizontal axis is still spatial so transforming all pixels will result in a

spectrum resolved in time, frequency, and one spatial dimension. For many experiments, the spatial dimension is not necessary so the detector elements can be binned across rows yielding a large signal increase over use with a monochromator where binning horizontally would eliminate spectral information. Additionally, at 2 nm resolution, an aperture of several mm can be used in an interferometer as opposed to an 80μm input slit for the monochromator giving the FT method a much higher throughput. A disadvantage of the FT method is that multiple shots and streak camera images are required to generate the interferogram making the method more susceptible to long term instabilities than the dispersive method which generates the entire data range with each image, albeit at lower S/N.

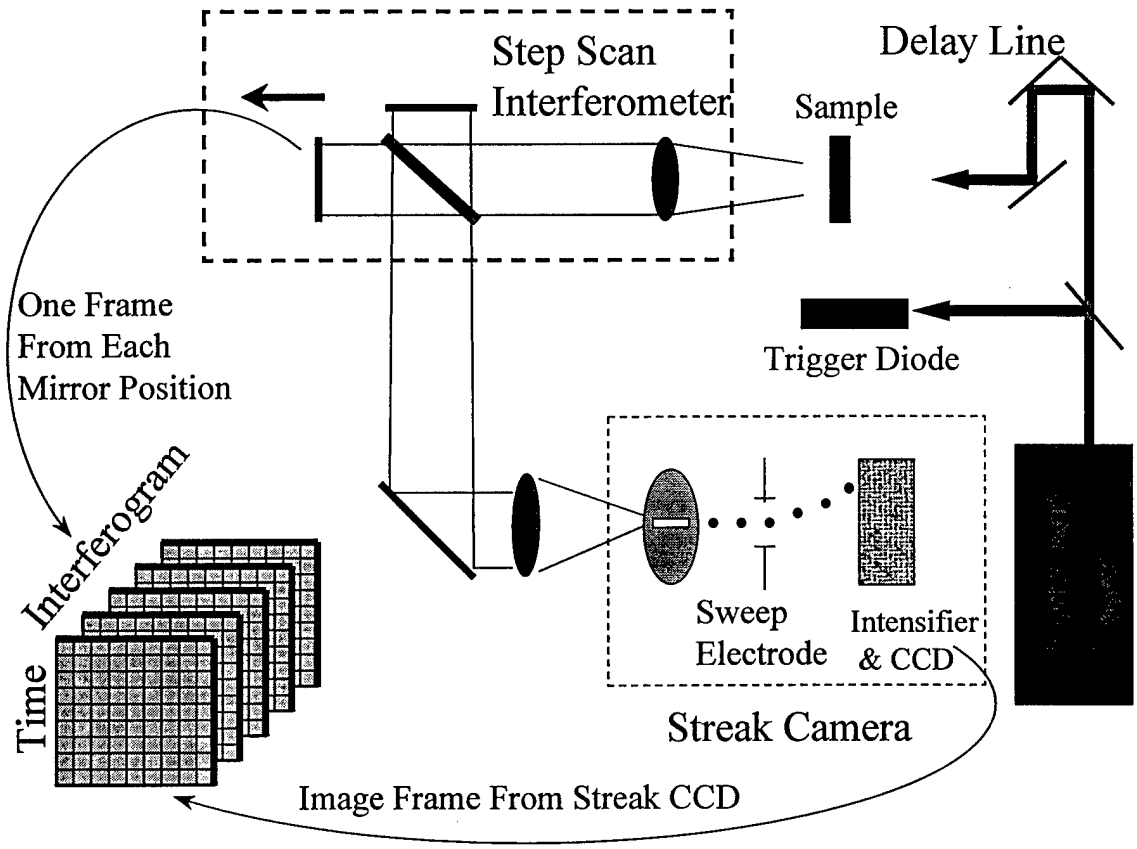

Figure 9. Ultrafast time and frequency resolved spectroscopy with a streak camera and a step-scan interferometer. A streak image is acquired at each mirror position of the interferometer. The result is a data cube with time on the vertical axis, a spatial dimension on the horizontal axis, and an interferogram across the images. Binning the horizontal dimension and Fourier transforming across the images results in a time and frequency resolved spectrum with up to 2 ps resolution.

We have successfully acquired time and frequency resolved ***emission*** from an oligimer in solution. Figure 10 shows streak camera images from two adjacent mirror positions in the vicinity of the zero path difference (the "centerburst" region where the greatest intensity variation occurs). The pixels were binned horizontally then Fourier transformed across all mirror positions to yield the time and frequency resolved spectrum shown in Figure 11.

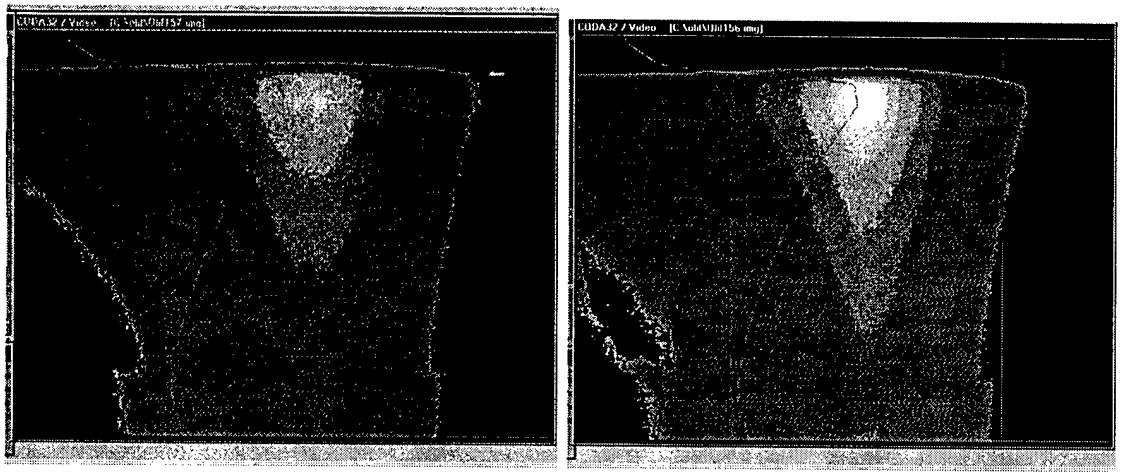

Figure 10. Streak camera images from two adjacent interferometer mirror positions near the "centerburst" of the interferogram. The difference in intensities is due to different degrees of positive interference.

This data shows emission induced by excitation with 200 fs pulses at 400 nm. While the data is presented at 100 ps / trace for clarity, it was acquired with 10 ps resolution and up to 2 ps is possible for the system. This experiment provides proof of principle for the funded facility and to our knowledge, we are the only group that has interfaced a streak camera to a Fourier transform spectrometer to perform ultrafast time and frequency resolved spectroscopy. Work is ongoing to apply this method to PIA spectroscopy.

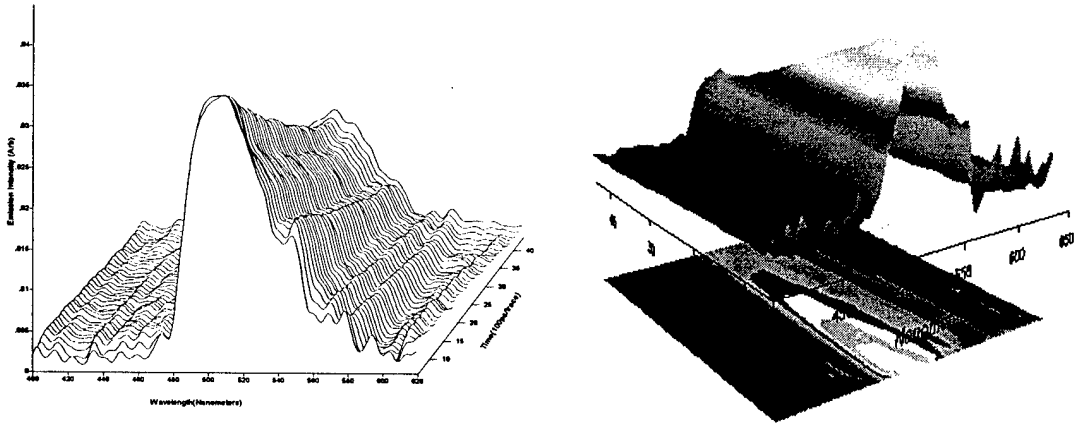

Figure 11. Time and frequency resolved emission from an organic chromophore on the sub-ns time-scale using a streak camera and step-scan interferometer. The resolution is approximately 20 ps and up to 2 ps resolution is possible by this method.

Papers published with the help of this facility.

"Fourier Transform Techniques for Measuring Absorption of Transient Species in Optical Limiting Materials" Y. Han, W. Sonnenberg, K. Short, and L.H. Spangler, *Proceedings of SPIE* **3798** In Press.

"Photo-Induced Effects In Mn^{4+}:Yag. Observation Of Unusually Efficient Excited State Absorption And A Long - Lived Metastable State." Yanong Han, Lee H. Spangler, Ralph Hutcheson, And Randy W. Equall, *Materials Research Society Fall 1999 Conference Proceedings* In Press.

"Fourier Transform Techniques For Measuring Absorption Of Transient Species In Optical Limiting Materials" Yanong Han, Wendi Sonnenberg, Kurt W. Short, Amy Hyfield And Lee H. Spangler, *Materials Research Society Fall 1999 Conference Proceedings* In Press.

"Excited State Absorption In Dendrimers Incorporating Diphenylaminodiphenylpolyene Moieties Via Photo-Induced Electron Transfer" W. Sonnenberg, A. Hyfield, K. Short, L. Spangler, C. Spangler, *Materials Research Society Fall 1999 Conference Proceedings* In Press.

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