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14. ABSTRACT
An apparatus capable of producing and detecting neutral ozone species created from high pressure oxygen using strong field photonic reagents have been designed, constructed, and utilized. The apparatus uses femtosecond BoxCARS to probe small volumes with multiple laser beams. Using this technique, strong evidence was obtained that photonic reagents convert O2 to conventional ozone. Progress has also been made on the understanding and control of filament formation in ambient conditions. For guiding the search for appropriate photonic reagents, the use of dimensionality reduction schemes was demonstrated on several model systems; the software code was developed that is used for reducing the complexity of the search space near dimension of 64. A general intrinsic parameter extraction method was developed for nonlinear cases; it may enable control independent of the measurement settings. Quantum control landscapes for photonic reagent optimization were shown to be trap free and inherently robust, thereby permitting optimization searches to reach the ultimate yield and to effectively manage experimental noise even near the top.

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FINAL PERFORMANCE REPORT

Project Title: *Photonic Reagents: The Production of Cyclic Ozone, With a Focus on Developing Equation Free Methods for Optimization Schemes*

Contract/Grant #: FA9550-05-1-0039
Reporting Period: 1 December 2004 to 31 December 2007

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Objectives

The key milestone of this project will be the demonstration of the formation of cyclic ozone using an intense, shaped laser pulse as detected by analytical methods including coherent anti-Stokes Raman spectroscopy. The quantitative goal was to create 10^{15} cyclic O_3 per second given an interaction volume containing 10^{18} conventional ozone molecules.

The second milestone was the development of enhanced software and algorithms to speed the evolutionary search process. The notion was to provide substantial improvements to the computer code that is used to control the laser pulse shaping system via the incorporation of optimization via model-free calculus.

Accomplishments/New Findings

During the tenure of this award several major objectives were realized. The first was the design construction and utilization of an apparatus capable of producing and detecting neutral ozone species created from high pressure oxygen using strong field photonic reagents. The reagents are produced using optical pulse shaping of ultrafast Ti: Sapphire laser pulses of duration ~45fs. The intense shaped laser pulses are focused into an atmospheric pressure of O_2 to create new chemical products. The photonic reagent reaction products are detected using a new type of coherent anti-Stokes Raman spectroscopy (CARS) developed as part of the project mission. The description of the new apparatus has been published in the Journal Chemical Physics and Optics Letters.

Using this apparatus the milestone of converting neutral O_2 to neutral, bent O_3 has been achieved. The description of this series of experiments is being prepared for submission to Physical Review Letters.

The second major objective of the research program was the development of mathematical models and methods to understand and accelerate the optimization procedure for guiding the search for appropriate photonic reagents. The applied mathematics efforts ranged from fundamental studies of the nature of the optimization process, to the development of dimensionality reduction tools such as diffusion mapping and wavelet methods for optimization. A method was identified for actively managing a detection scheme and the statistical foundation for this method was delineated and is currently in press in the Journal of the Optical Society of America. Finally, a covariance mapping method was published to identify controllable channels in a complex quantum system. Both methods contribute to optimal, on the fly detection of molecules.

Summary of significant findings:

The research for the DARPA award from the CHEMS Program in the Microsystems Technology Office has resulted in numerous breakthrough technologies for Chemical Engineering at the Micro-Scale. These breakthroughs have occurred both at the level of experimental control and detection of neutral products for molecules with Hamiltonians tuned using intense shaped laser beams and at the level of integrated sensing and processing.

Temple University Effort:

Development of a three beam femtosecond boxCARS system for ultrafast CARS measurements[5,7]

We have developed both the experiment and theory necessary to perform femtosecond BOXCARS .In many of the emerging remote sensing efforts, probing a small volume with multiple laser beams is an essential element for successful implementation. Optically we have produced an apparatus that can observe the course of a reaction on the hundred femtosecond time scale by probing the vibrational structure of an evolving molecule.

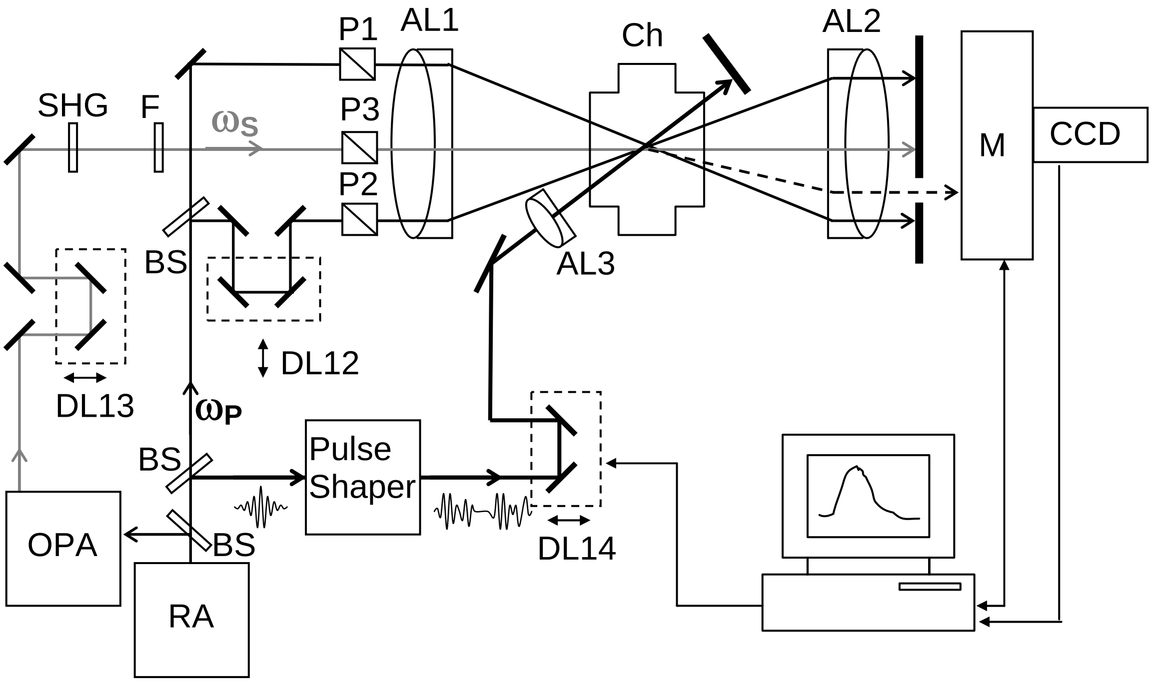

Figure 1. Experimental setup. AL – Achromatic Lens, BS – Beam Splitter, Ch – Chamber, CCD – CCD camera, DL – Delay Line, F – Filter, M – Monochromator, OPA – Optical Parametrical Amplifier, PMT – Photomultiplier, RA – Regenerative Amplifier, SHG – Frequency Doubler.

The method was recently described in a series of papers published in the Journal of Physical Chemistry and in Optics Letters. The papers outlined the methods necessary to suppress nonresonant contributions and to accurately describe the line shape resulting from the spectrally resolved CARS emission beam as a function of Stokes photon detuning.

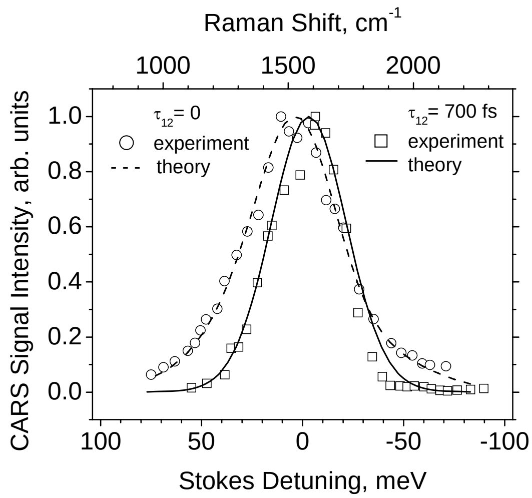

Figure 2. CARS spectra of the oxygen vibrational transition $\Delta G_{01} = 1556.4$ cm^{-1}. Circles are experimental points for time delay between pump pulses τ_{12} = 0 (nonresonant background is not suppressed) with the dashed line representing the theoretical fit obtained with our model. Squares are experimental points for τ_{12} = 700 fs (nonresonant background is suppressed) and the solid line is the corresponding theoretical fit.

Each of these effects are necessary for accurately making calls regarding the presence or absence of a CARS feature in a given vibrational signal. These results are of interest to other programs at DARPA, particularly the FASTREAD and RIEDAR efforts underway currently.

Multiplex BoxCARS[5,7]

The next major experimental break through was the interfacing of the new 3 beam fs BOXCARS method with an optical system that could detect all of the emitted CARS light simultaneously. This was accomplished by incorporating a high resolution Peltier-cooled CCD array spectrometer into the CARS detection system. This allowed us to rapidly detect the products of reaction.

The reactions under our control effort are accompanied/assisted/enabled by the formation of a filament of highly nonequilibrium plasma, so that the reaction dynamics is intertwined with the ultrafast dynamics of essentially inhomogeneous plasma.

Develop methods to interpret 3D CARS spectra (ω_{CARS},, $\omega_{detuning}$,, t_{delay})[5,7]

In the process of measuring the 3D spectra, many features were observed that, at the time, were not understood. These included features arising from CARS from molecules, atomic emission lines, nonresonant CARS and four wave scattering from plasma. The understanding of the spectroscopy of the CARS experiment as performed on the laser-induced filament/plasma is essential for performing the intended cyclic ozone experiment, the spectra are complicated and required the development of new theoretical insight to interpret.

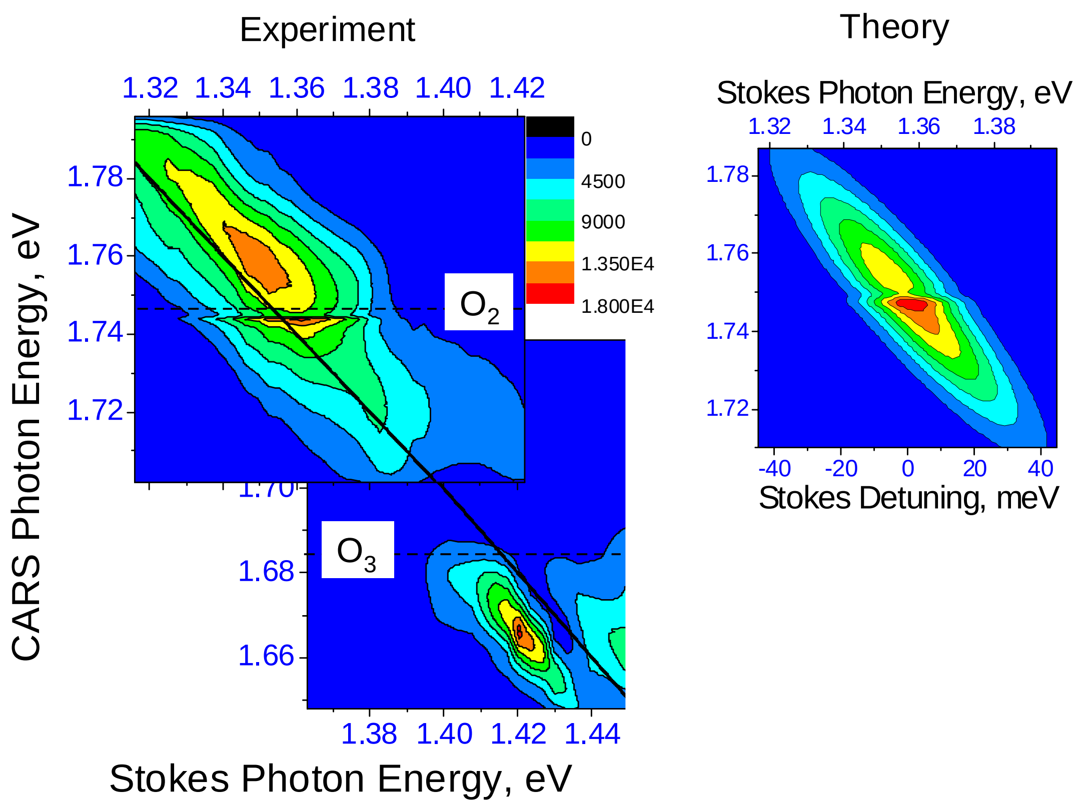

Figure 3. 3D CARS spectra of the oxygen vibrational transition $\Delta G_{01} = 1556.4$ cm^{-1}, corresponding to $\hbar\omega_{Stokes}$ = 1.357 eV, measured in plasma generated by a laser pulse at a time delay of τ_{14} = 120 ps after plasma creation. Dashed lines denote positions of O_2 and O_3 resonances (independent of Stokes detuning). Solid line corresponds to the expected position of the nonresonant signal (or, in presence op plasma, much stronger plasma signal). Both O_2 and O_3 resonances demonstrate strong decrease of the signal above the resonance (destructive interference) and increase of the signal below the resonance (constructive interference). The plot on the right shows the simulation by means of our theoretical model.

Time-resolved measurements of laser-induced filament formation dynamics

The ability to detect such products with high sensitivity and selectivity has resulted in another break through measurement, the ability to probe the dynamics of filament formation on the time scale from femtoseconds to nanoseconds. This has allowed us to systematically study the laser-induced plasma formation processes for a wide variety of gases and as a consequence we have developed a predictive model for filament formation, intensity and time dynamics that is of great value for stand off detection experiments underway at DARPA (RIEDAR) and at JIEDDO (SHIELDS).

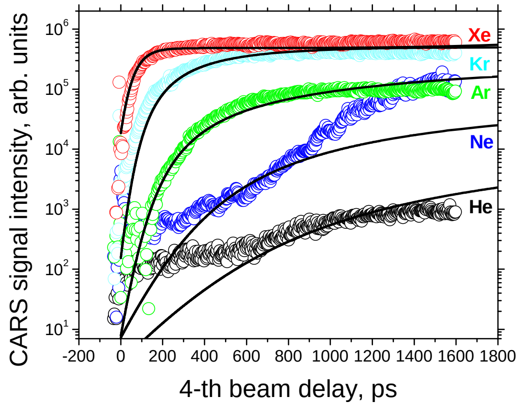

Figure 4. Dynamics of a non- degenerate Four-Wave-Mixing signal a from that is plasma created by a laser pulse. Data is presented for the first five noble gases. The circles represent experimental data, solid lines are simulated by means of our theoretical model.

There are presently two papers in press regarding this work describing the measurements and model for ultrafast laser filamentation in a series of noble gases and then comparing the dynamics in atomic and molecular systems. In this work we provide time resolved measurements of the four wave scattering probability as a function of time and the CW fluorescence intensity as a function of atomic IP. The latter measurements reveal that the excitation probability scales with ADK predictions for ionization probability and laser intensity.

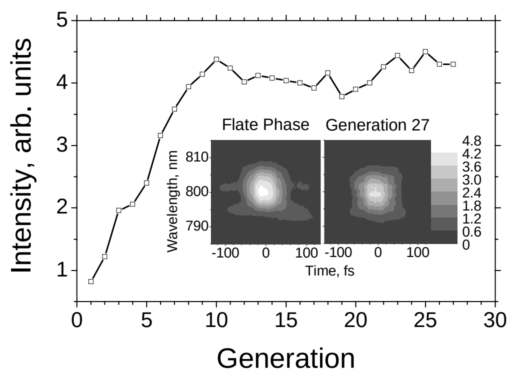

Figure 4. Optimization of the CARS signal near ozone resonance.

Photonic reagents with CARS detection for feedback control[1,3,4]

We employed the newly developed spectroscopic method to determine whether photonic reagents could transform an atmosphere of O_2 to ozone. In this experiment, the fs BOXCARS system was used as the feedback for driving the laser pulse shaping genetic search algorithm. The system was set to optimize signal in the spectral range where we expect the O_3 vibration. The system indeed optimized the ozone signal within 30 minutes and optimized on a known solution for the production of ozone. This was a transform-limited pulse. This experiment clearly needs to be reproduced using the new multiplexed CARS system as plasma background may have contributed to the feedback signal.

Software:

Several software programs have been written for use in the projects. The first is the diffusion mapping code that is used for reducing the complexity of the search space near dimension of 64. The second was code developed to record the femtosecond box CARS spectra used in the optimization procedure. The optimization code was also customized for the fs box CARS detection method.

Math Efforts: Dimensionality Reduction Schemes[2,6]

The applied mathematics efforts ranged from fundamental studies of the nature of the optimization process, to the development of dimensionality reduction tools such as diffusion mapping and wavelet methods for optimization. A method was identified for actively managing a detection scheme and the statistical foundation for this method was delineated and is currently in press in the Journal of the Optical Society of America. Finally, a covariance mapping method was published to identify controllable channels in a complex quantum system. Both methods contribute to optimal, on the fly detection of molecules. A method was developed to use statistical methods to determine the most controllable channels in an optimization experiment for molecular processes.

Considerable effort was expended on attempting to use dimensionality reduction algorithms to determine low dimensional structure in the otherwise high dimensional search space of the pulse shaper. Two experimental platforms were investigated in great detail, mass spectral fragmentation and second harmonic generation in a nonlinear doubling crystal. The latter experiment was performed in order to demonstrate that dimensionality reduction could be performed on a second order system where we could model the results of the interaction to the highest detail. Experiments were performed using randomly shaped laser pulses to induce doubling in a BBO crystal, and the amount of doubled radiation was scored as fitness by a photomultiplier tube. The system was also modeled numerically as the physics of second harmonic generation is extremely well-understood. In silico, pulse shapes were generated and the amount of doubled light theoretically predicted was also scored as the fitness for each laser pulse shape. As a handy dimensionality reduction technique, we chose the diffusion mapping: this direct (non-recursive) method proved efficient in uncovering low-dimensional manifolds in a number of applications. The novelty of our approach as compared to these earlier applications is that now an output parameter, the fitness, was included in the data specification on an equal footing with the pixel setting values thus forming an extra dimension. We have found that the diffusion mapping algorithm indeed generates low-dimensional representations of the random data set and thus provides insight into the control landscape and extrapolation to the highest-fitness point. However, these representations appear to depend essentially on the weighting factor assigned to the additional dimension (the fitness) in the data specification. Starting with some moderately large values of this factor, the fitness is so much amplified in comparison with the pixel setting values that it becomes the most important dimension in the map, thereby reducing the map to a one dimensional system, a line segment. This oversensitivity was also revealed in a control numerical experiment performed on the diffusion mapping of simple curves: a circle and then ellipses of increasing values of eccentricity. The circle and low-eccentricity ellipses regained their shape upon the diffusion mapping; however, starting with some critical value of eccentricity, the diffusion map of an ellipse snapped into parabola indistinguishable from a line segment representation. These results show that in its current form the diffusion mapping procedure is not robust enough to be used without adaptive adjustments of the proximity parameter in the diffusion kernel and the fitness weighting factor. The choice of these parameters depends on the sampling density and the complexity of the control landscape. Despite these shortcomings, the diffusion mapping technique, when equipped with back-projection into the original data space, may serve as a helpful preprocessing tool for genetic search algorithms.

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Yale University and Plain Sight Systems Effort:

We have through extended collaboration with the Temple and Princeton teams developed a number of empirically driven control mechanisms for driving light pulses.

Specifically, diffusion based analysis as described in our papers enables an empirical identification of local control variables, this organization is driven by both the objective function (or functions) and by the data generated through the experiment.

We address here the mathematical advances and refer to the Temple and Princeton groups for further results and applications.

1. A multiscale methodology for out of sample extrapolation was developed, this is a fundamental enabling tool to compute surrogate empirical gradients for driving optimization. It also enables the definition of control parameters.[1-4]
2. An intrinsic parameter extraction methodology extending independent component analysis to the nonlinear case was discovered and developed. In principle this method enables discovery of control parameters independent of the measurements methodologies.[5,6]
3. A method to organize the geometry of data generated empirically incorporating the properties of objective functions was developed and tested extensively on CHEMS data as well as on complex simulated electromagnetic scattering configurations depending on 200 parameters, with remarkable success.[7]
4. A complete theory explaining the nature of the distribution of points driven by a randomized gradient descent process (Langevin equation) has been developed, to explain and quantify the empirical procedures mentioned above.[8]

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Princeton effort: Fundamentals of Optimal Control:

During the period of this research, several parallel activities were pursued resulting in significant advances in the capability for controlling quantum dynamics phenomena. These advances are summarized below.

<u>Why is it proving so easy to control quantum systems</u>[1-6]**?**

Counter to simple intuition and projections a number of years ago, it is in fact proving to be easy to control even complex quantum systems in the laboratory. Mounting numbers of experiments in many laboratories provide ample evidence for this statement. This aspect of the research delved into the reasons for this surprising and attractive behavior. A key finding lies in the topological nature of the control landscape, which is the observable as a function of the control field. Quantum control landscapes were shown to be trap free, thereby permitting optimal control searches to reach the highest levels of possible yield. A broad variety of mathematical analyses were carried out in this research identifying that control landscapes exhibit inherent degrees of robustness to control noise while climbing the landscape as well finally at the top. These collective findings provide a rigorous foundation for projecting a positive future for the field of controlling quantum phenomena, regardless of the application. Thus, we may conclude that only control resources (i.e., energy, bandwidth, etc.) limit the degree of attainable control.

<u>Laboratory control experiments</u>[7,8].

Building on the fundamental findings of the theoretical landscape research above, an experiment was carried out to establish the reality of these theoretical predictions. In particular, the control landscape analyses predict that level sets of equivalent control outcomes will exist throughout the landscape including at the absolute top. This assessment was verified in an experiment controlling second harmonic generation thereby providing a firm confirmation of the very positive theoretical analyses.

<u>Control of molecular isomerization and the creation of cyclic ozone</u>[9]**.**

One general goal of the overall research project was examine the use of shaped laser pulses (photonic reagents) as a means for converting ordinary ozone to its high-energy cyclic counterpart. Theoretical work was carried out exploring the feasibility of this transformation through consideration of the rearrangement process in the presence of a competing dissociation channel. This latter competition is a key issue for forming cyclic ozone, as on the way to this goal the break-up channel is ever present. The theoretical analysis and simulations showed that it is possible to overcome the break-up process through suitably tailored pulses. This work provides the basis for further laboratory exploration of the formation of cyclic ozone.

New control mechanisms and processes[10-12].

This aspect of the research explored a new algorithm for revealing control mechanisms, and a new means for practical implementation of control in the laboratory. In the first category, mechanism analysis of controlled quantum dynamics is a topic of broad general interest. An algorithm for mechanism identification was developed in this work and its experimental demonstration was quite successful. A second component of the research considered the prospect of controlling quantum systems using tailored incoherent sources. Although, this direction may appear counter the use of high technology femtosecond laser systems, it is exactly the complexity of these latter systems and their cost, which motivated the desire to explore this alternative route. In particular, it appears that good degrees of control may be achieved by utilizing optimally filtered incoherent broadband radiation sources, which are readily available. The practical implementation of this concept could have wide ranging applications for the field. A laboratory experiment is currently under construction to demonstrate this capability.

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Current Experiments

The formation of cyclic ozone:
At the present time we are preparing for experiments concerning the conversion of normal ozone to cyclic ozone using shaped photonic reagents. We have assembled the necessary spectroscopic detection technology and theory to actually make the correct assignment when the signal is detected. The technology and theory is described above.

Investigations of filament dynamics:
The system is also being employed to investigate the ultrafast time dynamics of filament formation and propagation. This is necessary as the present scheme for the creation of cyclic ozone involves the use of a micro plasma as created and manipulated by a shaped intense laser beam.

Diffraction from filaments:
In addition to the investigation of ozone in a laser-induced plasma, we have discovered that two filaments when crossed will form a diffraction grating that has sufficient contrast to diffract an incident laser beam. The apparatus is shown in the accompanying figure and consists of splitting the amplified laser beam in a Michelson interferometer and crossing the beams at and angle of 30 degrees. The filaments created by the laser beams are set to overlap spatially and temporally at the desired point in space-time. This arrangement creates a plasma grating in space that has a period characteristic of the laser frequency and angle of crossing. The plasma density modulation is given by Eq. A. A third ultrafast laser beam can then undergo diffraction if this beam arrives during the time that the grating exists. Initial experiments suggest that the grating will diffract for up to 20 ps after the initial laser pulses create the plasma.

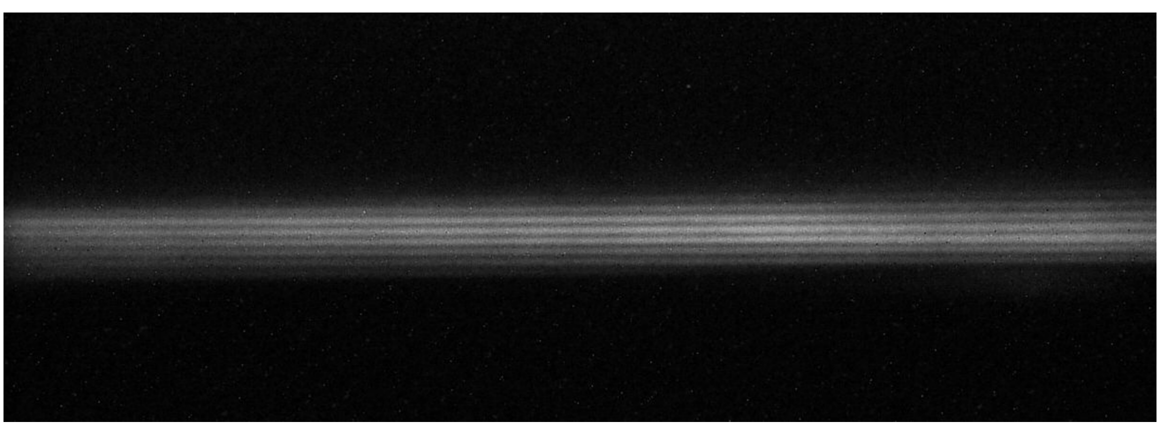

Figure 5. Microphotograph of plasma grating created by multiplex filament.

Stark-Modulated Fluorescence Emission:
Another consequence of the DARPA CHEMS project was the discovery of a method to induce Stark-modulated fluorescence emission lines up to 100 nm from the initial line position. In this work a weakly ionized plasma is used to induce fluorescence from a particular atom or molecule in the gas phase. Then a moderate field femtosecond laser pulse interacts with the plasma to induce shifts in the ground state of all atoms or molecules in the laser beam. Because the plasma is a black body emitter, one can induce amplified stimulated emission in the Stark shifted atoms that in turn leads to a bright laser-like beam of radiation in a particular direction. The amount of the Stark shift depends on the intensity of the laser beam and hence we can selectively shift fluorescence lines up to 100nm and take the otherwise isotropic emission and localize it into one particular direction. This may have major implications for photonic computing and communication schemes.

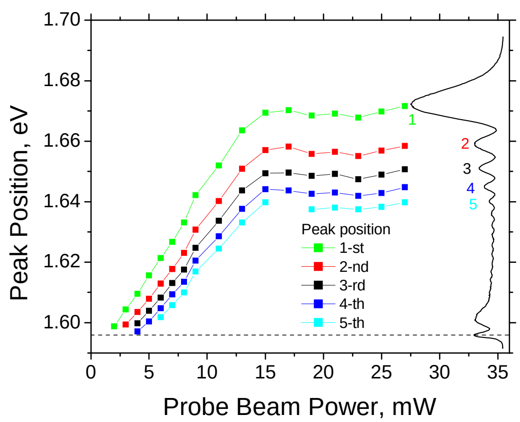

Figure 6. Spectrum of laser-like stimulated emission induced in plasma by probe laser beam (right side of graph). Squares show a Stark shift of emitted peaks as a function of probe beam power.

Leveraged Research Enabled by the CHEMS Effort:

There have been a number of efforts that have leveraged the findings, methods, expertise and theory developed as a result of this DARPA award. These include the two efforts presently underway as a result of JIEDDO funding. A team consisting of Temple University, Army Research Laboratory, Yale University, Proteus Optics and Plain Sight systems has formed to develop the "Shaped Intense Laser Detection and Surveillance" (SHIELDS) system for detecting improvised explosive devices. Another effort is underway that consists of the Team of Princeton University, Aeordyne, Army Research Laboratory to develop highly nonlinear detection systems for IEDS using the concept of optimal dynamic discrimination (ODD).

Another area that has leveraged the DARPA CHEMS program was the creation of a spin-off company, Proteus Optics, to make commercially available the laser pulse shaping optics, optimization code and the electronics necessary to interface the system to virtually any experiment. This company has recently designed a shaper that will handle up to 10mJ of amplified 800nm radiation. Current shaping systems can handle up to 0.5mJ at the present time.

The CHEMS effort has also contributed to our current effort to develop photonic enzymes, or laser pulses that will alter cell signaling pathways using only laser light and a target molecule in the cytoplasm.

The CHEMS system is currently in use to investigate and explore filamentation processes and filament induced diffraction gratings in air. As described, the latter may allow the observation of activities behind obstacles.

Technology Transfer to DoD and Industry:

The technology developed as a result of this DARPA project is available for other DoD efforts under way in the investigators laboratories. These efforts include an ARO MURI effort and an ARO STTR for the development of new pulse shaping systems. Two additional stand off detection efforts have been made as a result of JIEDDO funding. The developments in this research led to the initiation of a new JIEDDO program utilizing control concepts for the creation of high quality laser driven non-linearly operating detectors of explosive agents in the environment.

The extensive infrared handling methods developed specifically for the AFOSR/DARPA effort have assisted the development of a mid-IR pulse shaping system by the Company Proteus Optics, a spin off from the Center for Advance Photonics Research at Temple University.

Personnel Supported by the grant

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