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RPPR Final Report
as of 16-Sep-2019

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Major Goals: Our long-term goal is to develop and demonstrate the experimental feasibility to monitor sub-surface chemical reactions in scattering heterogeneous materials. We then plan to use this capability to investigate and characterize sub-surface chemical reactions in energetic materials.

Our initial focus is on developing and demonstrating the experimental capability to focus a laser beam inside a scattering heterogeneous medium and to perform Raman and LIF measurements at the focal spot. Once the feasibility of local sub-surface spectroscopy measurements has been demonstrated, we will evaluate the system for monitoring dynamically-changing conditions at the focal spot.

Accomplishments: • We demonstrated focusing onto a fluorescent bead embedded in a heterogeneous material using our single-SLM system.
• We characterized the performance of three different optimization algorithms (Iterative, Simple Genetic, and Microgenetic) for fluorescent feedback.
• We demonstrated improved fluorescent signal when performing bidirectional focusing utilizing a two-SLM focusing system.
• We obtained all the components required for the full optical setup.
• We constructed the full isotropic microscope with both wavefront shaping and digital optical phase conjugation (DOPC). Fine alignment is still in progress.
• We also completed the required programming for the full system (wavefront shaping and DOPC combined).

Training Opportunities: Dr. Benjamin Anderson continued to refine his optical skills with respect to combining wavefront shaping with digital optical phase conjugation.

Two undergraduate students, Ms. Rebecca Tucker and Mr. Kostiantyn Makrasnov, provided programming support to ensure the various pieces of equipment can be centrally controlled. In addition to working for the first time in a research-driven environment, the work itself was a new experience for both of them.

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

RPPR Final Report
as of 16-Sep-2019

Protocol Activity Status:

Technology Transfer: Nothing to Report

PROBING SUB-SURFACE REACTIONS IN THE CONDENSED PHASE VIA RAMAN AND LASER-INDUCED FLUORESCENCE SPECTROSCOPY

W911NF-18-1-0189

Final Report

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I. BACKGROUND

Washington State University (PI: Dr. Hergen Eilers) is currently funded by the ARO (Grant no. W911NF-18-1-0094), to develop a technique for probing sub-surface reactions in the condensed phase via Raman and laser-induced fluorescence (LIF) spectroscopy.

The need for such measurement capabilities is driven by the need to better understand energetic materials. Explosives and propellants are heterogeneous materials consisting of energetic molecular crystals embedded in polymeric binders. These energetic materials can be initiated through a variety of stimuli, including thermal, mechanical, and electrical means, with the non-thermal stimuli believed to generate heat first which then causes thermally induced chemical decomposition.

Optimizing the performance of energetic materials for specific applications must be balanced against safety and reliability considerations. This process requires an improved fundamental understanding of the chemical reactions inside the material. In particular, the need for real-time monitoring of local sub-surface chemical reactions in energetic materials is well recognized. However, the challenging nature of this problem has precluded significant success to date.

II. GOAL

Our long-term goal is to develop and demonstrate the experimental feasibility to monitor sub-surface chemical reactions in scattering heterogeneous materials. We then plan to use this capability to investigate and characterize sub-surface chemical reactions in energetic materials.

Our initial focus is on developing and demonstrating the experimental capability to focus a laser beam inside a scattering heterogeneous medium and to perform Raman and LIF measurements at the focal spot. Once the feasibility of local sub-surface spectroscopy measurements has been demonstrated, we will evaluate the system for monitoring dynamically-changing conditions at the focal spot.

III. APPROACH

To achieve our objectives, our main focus is on developing, evaluating, and optimizing a microscope with isotropic focusing and bidirectional optical phase correction. A guide-star (e.g., fluorescent particle) will be used in conjunction with a spatial light modulator (SLM) to focus the laser beam inside the scattering sample. A second objective collects the forward scattered light and guides it to a detector, which in conjunction with a second SLM generates an optical phase conjugate and focuses the light back into the sample. Raman scattered and/or fluorescent light is collected by the first objective and guided to a detection system. The use of two objectives in combination with the optical phase conjugation allows for distortion correction and focusing inside a scattering medium. Isotropic focusing using two opposing objective lenses has been shown to result in focal spots of reduced axial size, while OPC compensates for scattering and the need to exactly align the two lenses [1]. Using this approach, Jang et al. demonstrated that the axial focal size was reduced by more than a factor of 4 [1].

Our proposed approach expands on the work of Jang et al. [1], and Figure 1 shows a schematic of our modified setup. In the first step, one of the laser beams is focused into the sample using objective 1 via a reflective spatial light modulator (SLM 1). This step requires that the sample contains a guide-star (e.g., fluorescent marker, second harmonic generator, etc.). An optimization algorithm is used to focus the light onto the guide-star, located inside the heterogeneous sample, by optimizing the fluorescence intensity measured by CCD 2. Once that is accomplished, the SLM 1 settings (i.e., the optimized wavefront) remain fixed.

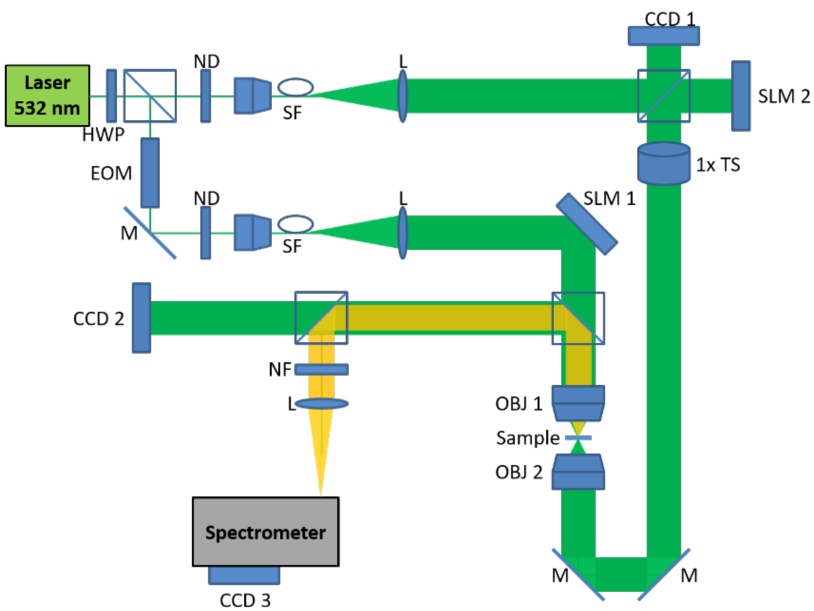


Figure 1. Schematic of proposed setup for probing sub-surface reactions via Raman and LIF spectroscopy.

Objective 2 collects the forward scattered light and guides it toward a detector (CCD 1). This light is then overlapped with a reference laser beam to generate an interference pattern on CCD 1 and to determine the scattered light's wavefront. This information is then sent to a computer which controls a second spatial light modulator (SLM 2). SLM 2 generates a phase conjugated beam and sends it back to the sample using objective 2. The result is an isotropically focused laser spot in the sample combined with a phase modulated beam that compensates for scattering in the sample.

Signal light from the focal spot is collected via objective 1 and guided via various optical elements into an imaging spectrograph with attached detector (CCD 3). This setup would allow us to focus the laser beam inside the sample without interference from scattering, and to characterize sub-surface sample volumes via Raman scattering and LIF.

In order to develop the proposed experimental microscope with isotropic focusing and bidirectional optical phase correction and to demonstrate its feasibility, a variety of research activities will be conducted, including: (i) assembling the optical setup; (ii) developing and evaluating an optimization algorithms suitable for focusing light into a scattering medium, and for generating the phase conjugate of scattered light; (iii) preparing samples consisting of polymeric binders with scattering organic molecular crystals and a fluorescent particle; (iv) focusing light inside a heterogeneous medium; and (v) evaluating the limitations of the system..

IV. EQUIPMENT NEEDS

While we have a laser, several CCDs, one SLM, and various optical components, the proposed microscope with isotropic focusing and bidirectional optical phase correction setup shown in Figure 1 requires a second SLM, a spectrograph with optimized detector for Raman and LIF measurements, objectives, position-controlled stages for the objectives and sample, and several other optical components.

Funding for the following items was requested to complete the microscope with isotropic focusing and bidirectional optical phase correction setup:

	Description	**Model #**	**QTY**	**Vendor**	**Budget**	**Estimated useful life**
1	Spectroscopy system	Multiple	1	Princeton Instruments	$94,195	10 years
2	Ultra-High-Speed OverDrive Plus 512 x 512 Nematic SLM System	ODP512-0532-P8	1	Meadowlark	$19,575	10 years
3	EO Modulator, power supply, and 3-Axis RollerBlock Long-Travel Bearing Stage	Multiple	1	Thorlabs	$10,342	10 years
4	Two 100X Mitutoyo Plan Apo HR Infinity Corrected Objectives	58-238	2	Edmund	$11,126	10 years
5	NanoCube® XYZ Piezo Positioning system and LVPZT Piezo Amplifier	Multiple	1	Physik Instrumente	$8,680	10 years
	Total				**$143,918**	10 years

Actual expenditures are shown below:

	Description	**Model #**	**Vendor**	**Budget**
1	Spectroscopy system	Multiple	Princeton Instruments	$94,167.20
2	Ultra-High-Speed OverDrive Plus 512 x 512 Nematic SLM System	ODP512-0532-P8	Meadowlark	$19,725.00
3	Computer to control SLM	Precision Tower 3620	Dell	$1,674.06
4	Phase Mod, Nanomax stage, piezo controller, Amplifier, Rollerblock/Diff Drive	Multiple	Thorlabs	$18,186.27
5	Two 100X Mitutoyo Plan Apo HR Infinity Corrected Objectives	58-238	Miller	$9,519.00
6	Optics and other equipment for the DOPC microscope: beamsplitter, achromatic doublets, polarizer, mirrors, etc.	Multiple	Thorlabs	$646.47
	Total			**$143,918**

V. USE OF EQUIPMENT

A. Research work described in proposal

a. Single SLM Focusing

Our first accomplishment was demonstrating focusing onto a fluorescent bead embedded in a heterogeneous material using our single-SLM system. Figure 2 shows intensity profiles for feedback assisted focusing using both reflective (a,b) and fluorescence feedback (c,d). In reflection we focus into a single reflection mode making a small spot, whereas fluorescence focusing focuses on a 1-5 μm diameter bead, which results in a significantly larger spot size.

Having considered the intensity patterns for the two feedback mechanisms we next compared their enhancement curves as a function of iteration (using a simple genetic algorithm), which are shown in Figure 3. From Figure 3 we find that using reflective feedback we are able to obtain a larger enhancement, but also find that it takes more interactions to reach the final enhancement. Both the lower enhancement and faster convergence in reflection are due to the multi-modal optimization involved with fluorescence feedback. Lower enhancements when performing multi-modal optimization is a well-known phenomenon [2].

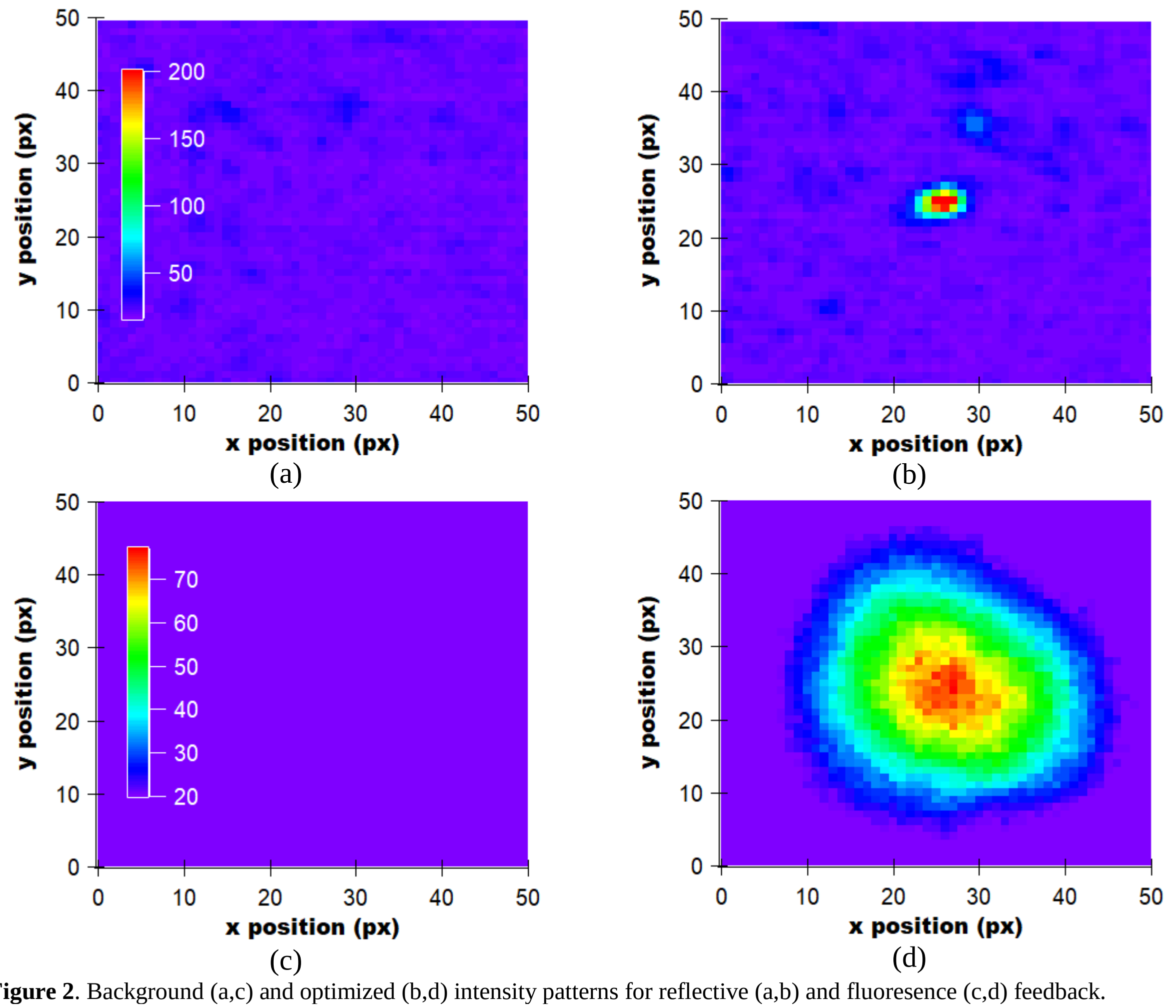


Figure 2. Background (a,c) and optimized (b,d) intensity patterns for reflective (a,b) and fluoresence (c,d) feedback.

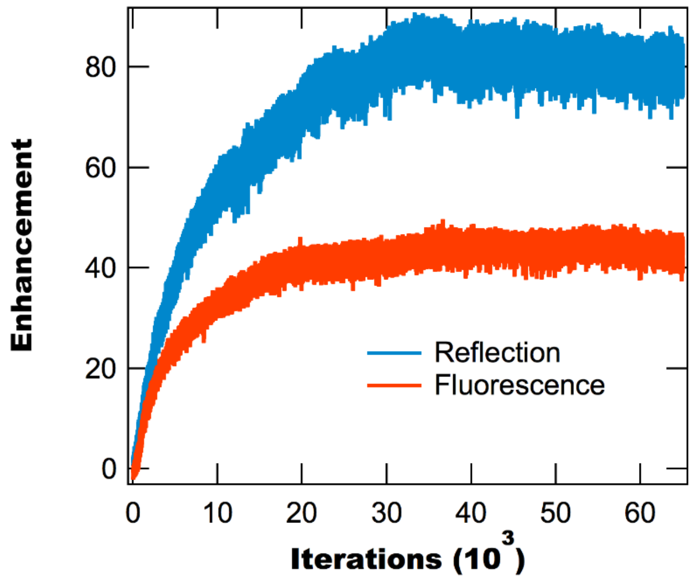


Figure 3. Enhancement as a function of iteration for fluorescence and reflective feedback. Optimization was performed using the SGA with 4096 bins.

After demonstrating single-SLM focusing onto a fluorescent bead embedded in a heterogeneous material, we next tested the performance of three different algorithms used for focusing: the iterative (IA), the simple genetic (SGA), and the microgenetic (μGA). Figure 4 shows a comparison of enhancement curves for all three algorithms with the μGA found to be the fastest and the SGA found to reach the largest enhancement. To quantify the speed of each algorithm we consider the number of iterations required to reach 90% of the enhancement curves final value and find the μGA to take 2990 iterations, while the SGA takes 15907 iterations and the IA takes 32109. These results translate into the SGA being 2 times faster than the IA, while the μGA is 5.3 times faster than the SGA and 10.7 times faster than the IA. These results are consistent with our previous algorithm comparisons using reflective feedback [3].

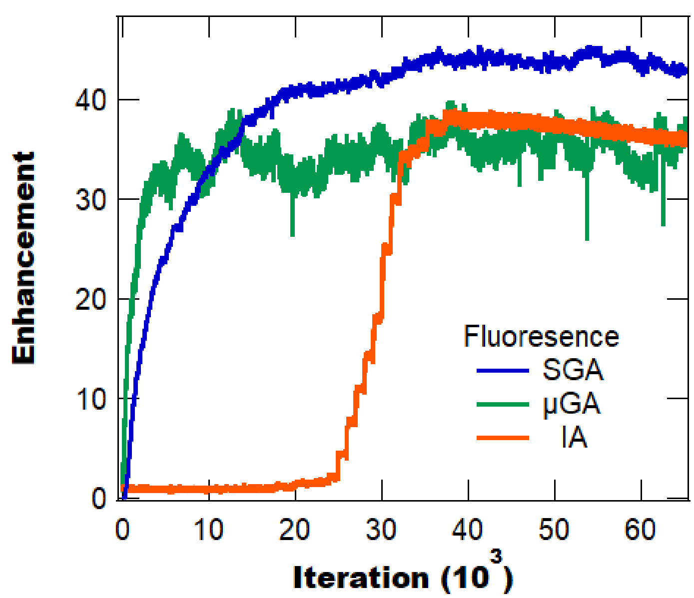


Figure 4. Fluorescence enhancement as a function of iteration for three different optimization algorithms and N = 4096 bins.

Having considered the relative speed of the three algorithms we next turn to considering the influence of the SLM bin size on the enhancement and calculation time for the two genetic algorithms. Figure 5 shows both the enhancement (a) and iteration time (b) for both genetic algorithms as a function of the number of bin numbers for optimization runs lasting 20000 iterations. From Figure 5a we find that the highest enhancement is obtained using the SGA with bins of size 4 px, which corresponds to 16384 bins. We also find that both GAs have similar performance for bin sizes ≥ 16 px. On the other hand from Figure 5b we find that while the calculation time for the µGA doesn't change much with increasing number of bins, the SGA suffers significant speed loss for bins < 4px.

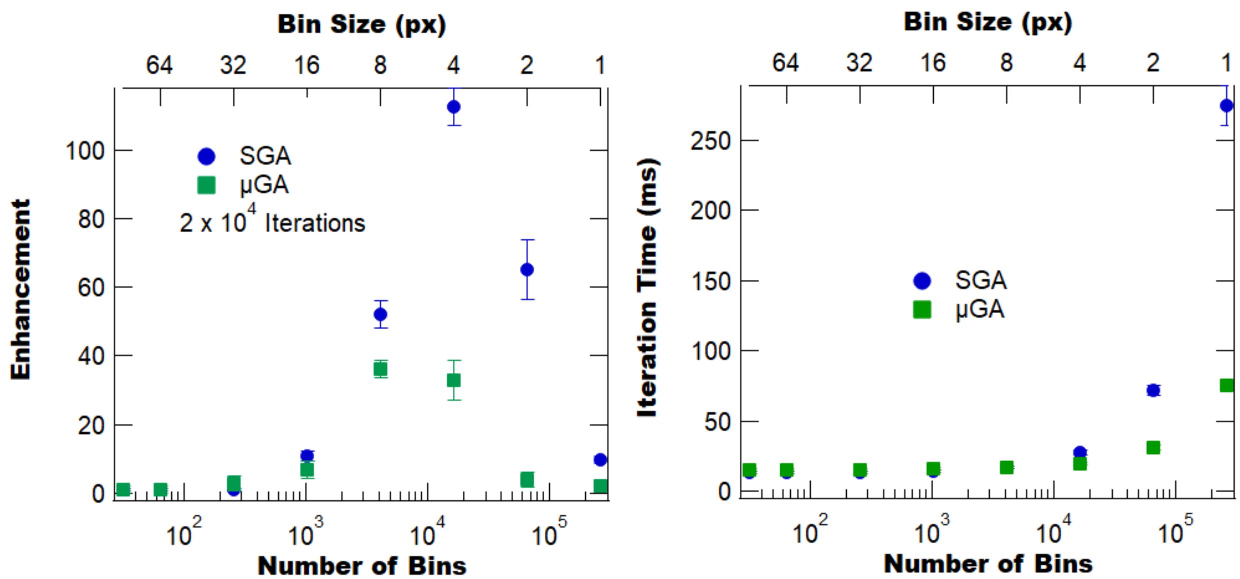


Figure 5. Enhancement (a) and Iteration time (b) as a function of the number of bins for both the SGA and µGA.

The last algorithm comparison we perform is to consider the effect of noise on the enhancement for each algorithm. For this measurement we perform optimization using all three algorithms with 4096 bins and add noise to the algorithm using a random number generator. Figure 6a shows the average enhancement curves as a function of iteration for 6 different noise levels (quantified by the standard deviation divided by the mean intensity) using the SGA and Figure 6b shows the final enhancement as a function of noise level for the three algorithms. Based on Figure 6 we find that the SGA has the best resilience in the presence of noise, followed by the µGA and then the IA.

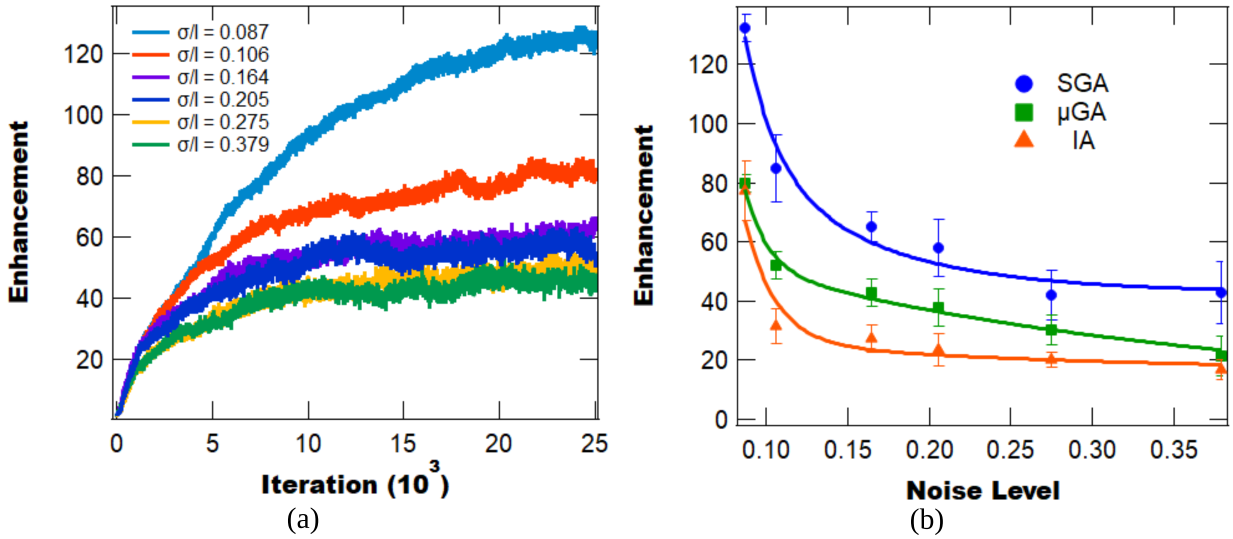


Figure 6. Enhancement as a function of iteration (a) and noise level (b).

b. <u>Feedback Assisted Bidirectional Focusing</u>

After demonstrating feedback assisted focusing inside a heterogeneous sample using a fluorescent guidestar, we performed focusing using a bidirectional focusing setup using feedback assisted optimization for both directions. Eventually one direction will be replaced by DOPC, but as an example of bidirectional focusing we first use feedback assisted optimization in both directions. For this focusing we use the setup shown schematically in Figure 7.

To demonstrate bidirectional feedback assisted focusing we once again use a fluorescent guidestar embedded in a heterogeneous sample and utilize the SGA with 4096 bins for both SLMs. Figure 8 shows fluorescence intensity patterns for the unoptimized flat wavefronts, for a single

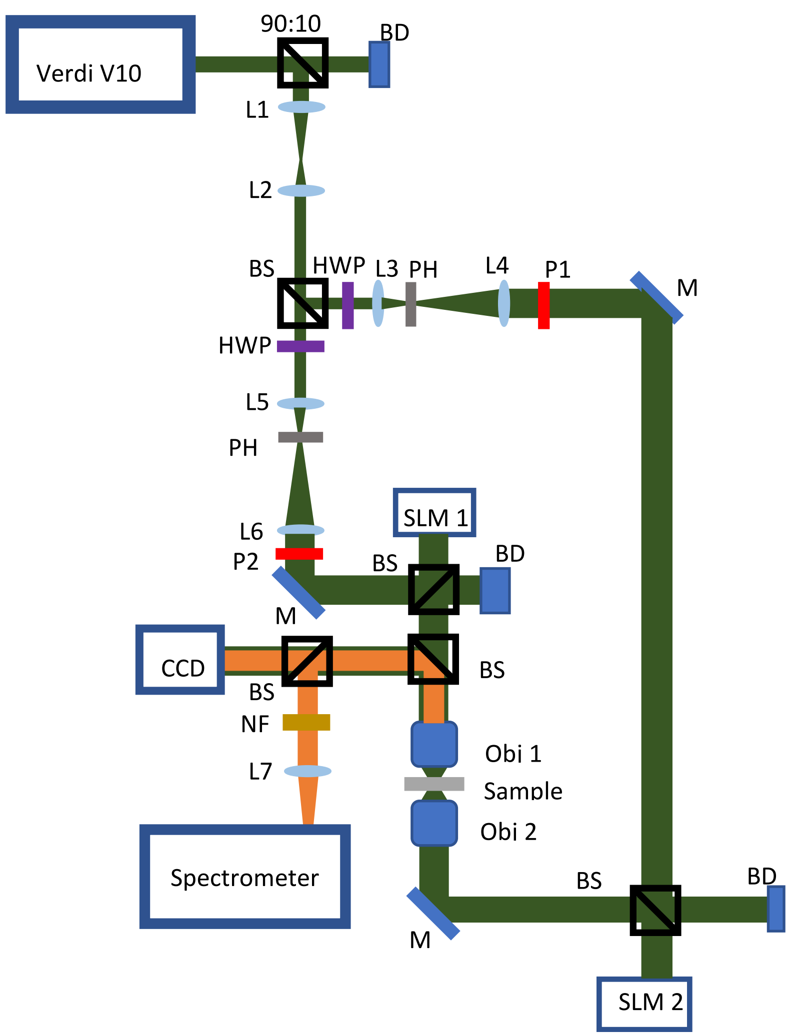


Figure 7. Feedback assisted bidirectional focusing setup schematic.

optimized SLM and two optimized SLMs (all images share the same intensity scale). From Figure 8 we find that by utilizing both SLMs we significantly improve the intensity from the fluorescent bead when compared to the single SLM system. This can be further demonstrated by taking line profiles of the intensity patterns, which are shown in Figure 9. From Figure 9 we find that there is significant improvement when using both SLMs over just using a single SLM. This highlights the benefits of utilizing bidirectional focusing for focusing inside heterogeneous materials.

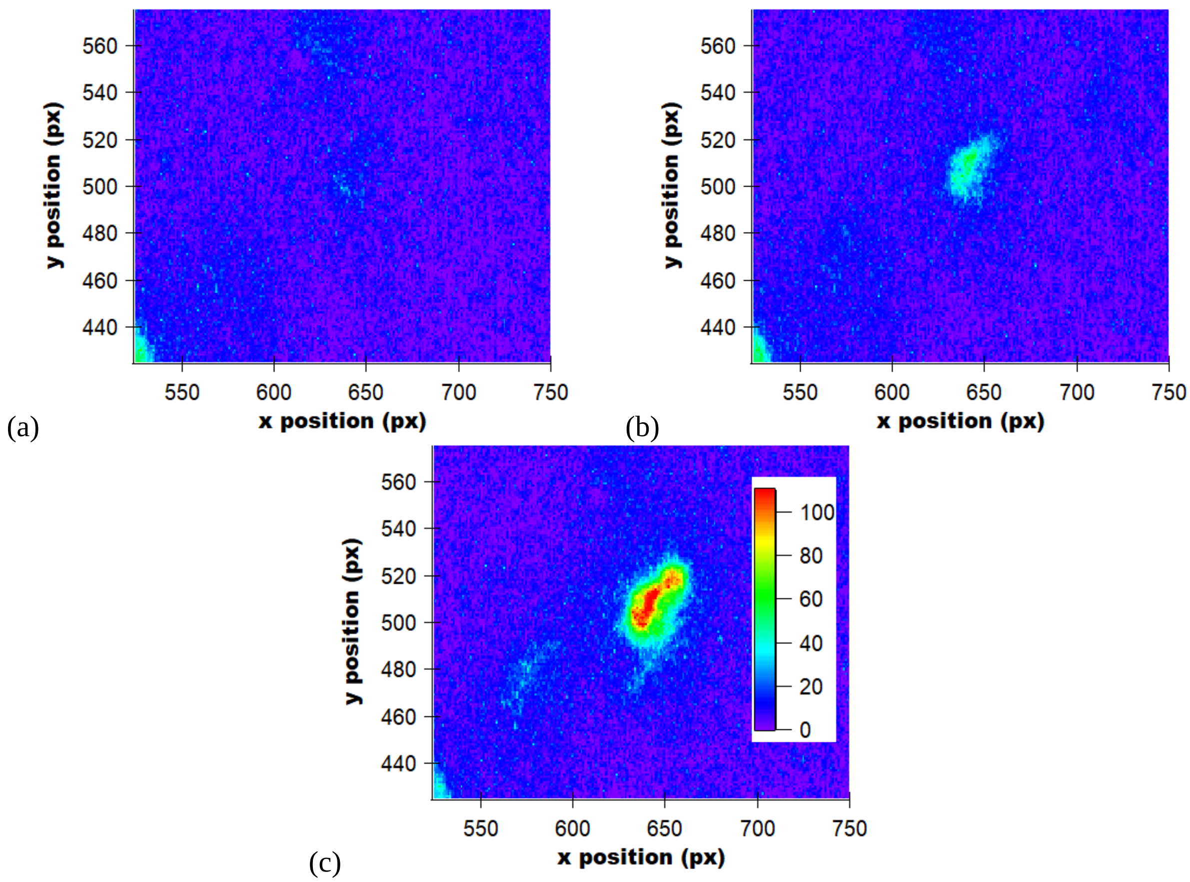


Figure 8. Intensity pattern for flat wavefronts (a), a single optimized SLM (b), and two optimized SLMs (c).

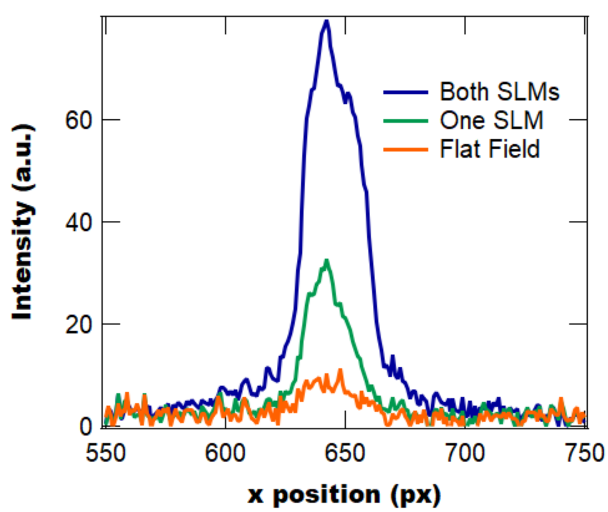


Figure 9. Intensity line profile for flat wavefront, single optimized SLM, and two optimized SLMs.

c. <u>Assembling DOPC System</u>

During the reporting period we purchased and received all the components necessary to build the full microscope with isotropic focusing and bidirectional phase conjugation. Figure 10 shows a schematic view of the system and a picture of the assembled system. In addition to assembling the hardware for the system we also developed the software necessary to run the system. However, we are still in the process of finalizing alignment of the system, which has proven to be very difficult. We are currently making several modifications to make alignment easier and hope to have the full system operational soon.

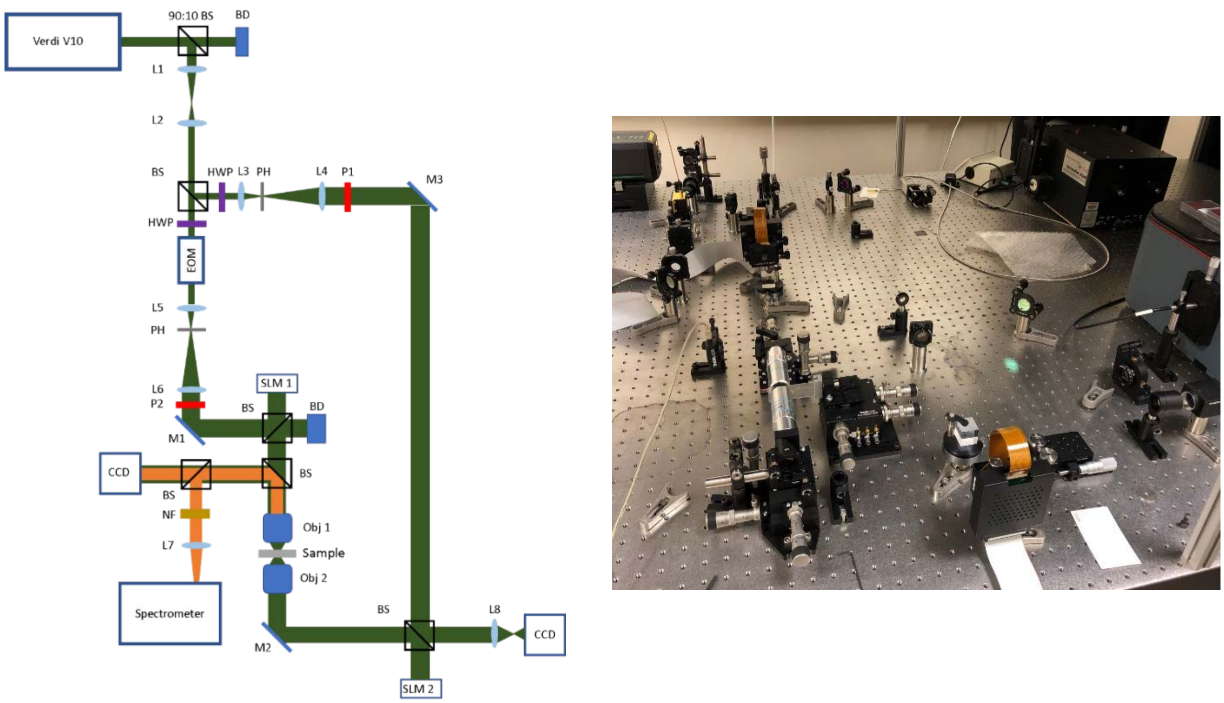


Figure 10. Schematic and picture of fully assembled microscope.

B. Other research of interest to DoD

Once operational, the microscope could be used for many other applications of interest to the DoD. For example, in the biomedical community, there is a large interest in focusing light inside tissue to characterize, monitor, and treat medical conditions.

VI. SUMMARY

Using the DURIP funds, we acquired all the required equipment and set up the experimental system. We then proceeded to demonstrated that, using our single-SLM system, we can focus a 532 nm laser onto a fluorescent bead embedded in a heterogeneous material. Next, we characterized the performance of three different optimization algorithms (Iterative, Simple Genetic, and Microgenetic) for fluorescent feedback. We then proceeded to set up the bidirectional focusing system, utilizing two SLMs, and demonstrated a significantly improved fluorescent signal. Subsequently, we integrated a digital optical phase conjugation (DOPC) system into the full isotropic microscope and used it in combination with wavefront shaping. Fine alignment of the full system is still in progress. In addition, we completed the required programming for the full system (wavefront shaping and DOPC combined).

VII. REFRENCES

[1] M. Jang, H. Ruan, H. Zhou, B. Judkewitz, and C. Yang, Opt. Express 22, 14054 (2014).

[2] I. M. Vellekoop, E. G. van Putten, A. Lagendijk, and A. P. Mosk, Opt. Express 16, 68 (2008).

[3] B. R. Anderson, P. Price, R. Gunawidjaja, and H. Eilers, Appl. Opt. 54, 1485 (2015).

Probing Sub-surface Reactions in the Condensed Phase via Raman and Laser-induced Fluorescence Spectroscopy, Hergen Eilers, WSU

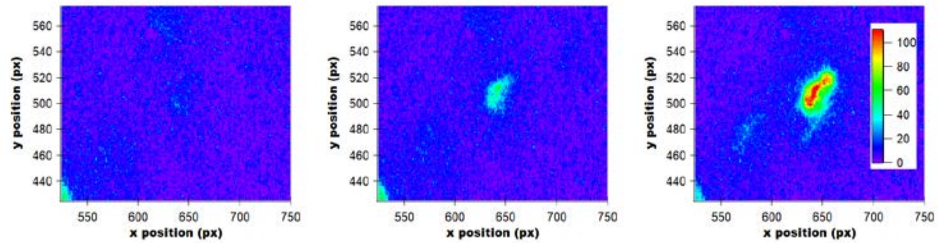
Objective:

Develop and demonstrate experimental feasibility to monitor in real-time sub-surface chemical reactions in scattering heterogeneous materials.

Scientific Challenges:

- How to focus light inside scattering medium?
- How to maintain focus and measure Raman spectra once chemical reaction starts?

Images of fluorescent particle in heterogeneous material



Flat Wavefront | Unidirectional Focusing | Bidirectional Focusing

Major Accomplishments:

- Demonstrated unidirectional focusing inside heterogeneous sample.
- Demonstrated bidirectional focusing inside heterogeneous material.
- Setup combined Wavefront Shaping (WFS) and Digital Optical Phase Conjugation (DOPC) system.
- Characterized different focusing algorithms.

Army Relevance: Better understanding of chemical reactions in energetic materials which could subsequently lead to better control and enhanced lethality and protection.

Funding profile:

FY18 $143,918

Grant # W911NF-18-1-0189

Dr. Hergen Eilers, Eilers@wsu.edu, 509-358-7681