LA-UR- 12-01313

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Intended for: SPIE Defense, Security and Sensing Conference, Baltimore, MD, April 23-27, 2012

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Optimal coherent control methods for explosives detection

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ABSTRACT

We are utilizing control of molecular processes at the quantum level via the best capabilities of recent laser technology and recent discoveries in optimal shaping of laser pulses to significantly enhance the detection of explosives. Optimal dynamic detection of explosives (ODD-Ex) is a methodology whereby laser pulses are optimally shaped to simultaneously enhance the sensitivity and selectivity of any of a wide variety of spectroscopic methods for explosives signatures while reducing the influence of noise and environmental perturbations. We discuss here recent results using the Gerchberg-Saxton algorithm to provide an optimal shaped laser pulse for selective coherent anti-Stokes Raman signal generation of a single component in a mixture.

Keywords: coherent control, dynamic nonlinear, ultrafast lasers, closed-loop optimization, detection, explosives

1. INTRODUCTION

Explosives are the key component of most violent threats the world faces today. Explosive materials are essential components of improvised explosive devices, suicide bombs, package bombs, and the means for dispersal of chemical, biological, or radiological compounds in dirty bombs. The first steps toward neutralizing these threats are detection and identification. For safety, it is desirable to be able to detect and identify explosives at large standoff distances; 50 meters is a common goal. Progress to date in developing fully capable trace and bulk explosives detection methods at standoff distances has been slow because: (a) only trace levels of observable material are available due to low explosives vapor pressures and/or small quantities of surface adsorbed explosive residues, (b) excitation of the sample must occur at a distance with subsequent return of the resultant radiative signature back to the detector, (c) operation must occur in the presence of atmospheric turbulence and particulate matter, (d) there are stringent demands for high sensitivity and high signal-to-noise and (e) high selectivity is needed to identify a given target material in the presence of possibly very similar but benign background chemicals. Unfortunately, many explosives have very low vapor pressures [1], making the detection of molecules in the air exceedingly difficult. One must then look for microscopic trace contamination that may have been left on an external surface, another challenging prospect. While there are a number of analytical methods that can be employed to detect and identify explosives, the number that are plausible at realistic standoff distances is far fewer [1,2]. Some of the most promising techniques rely on laser excitation, such as standoff Raman spectroscopy, standoff coherent anti-Stokes Raman spectroscopy (CARS), and laser induced breakdown spectroscopy (LIBS). Although there are numerous incremental improvements that can be made to current laser based standoff methods, the capabilities that are desired demand a revolutionary shift to higher levels of sensitivity and selectivity. Optimal Dynamic Detection of Explosives (ODD-Ex) is a novel framework for developing solutions to these seemingly impossible problems. A wide variety of complementary nonlinear optical methods are amenable to optimization using ODD-Ex tools. Results from one of these are discussed in this paper.

1.1 ODD-Ex and femtosecond pulse shaping

The essential ingredient of ODD-Ex is adaption of the interrogating laser to the quantum molecular dynamics of the target explosive. For any given laser/molecule nonlinear interaction leading to a signal, such as emission or ionization, there exists a pulse that will optimize that signal [3]. This optimal pulse is typically not what comes out of a commercial laser, but rather must be adapted to suit the specific molecule and spectroscopic signature of interest. There exists a strong theoretical foundation underlying both the existence of the optimal control field and a feature of the control search landscape suggesting that the optimal solution can be readily discovered [3,4]. Because the laser seeks to control the action of the molecules on their natural vibrational, rotational, and electronic timescales, a short pulse femtosecond laser is necessary. The best solution would be a laser system that could emit on demand one of the hundreds of different types of pulses in order to interrogate and detect the hundreds of desired explosive molecules. As yet, commercial lasers are not available with the appropriate pulses programmed in. Nevertheless, the technology already exists to shape femtosecond pulses into complex time-dependent optical fields. These techniques are now sufficiently mature to attack applied problems such as explosive detection.

To shape the femtosecond laser pulses, we utilize a programmable phase and amplitude mask located in the Fourier plane of a zero dispersion stretcher [5,6], which is in essence a subtractive double spectrometer with the mask placed at the central focal (Fourier) plane. At the mask, the colors are spatially separated and each spectral component passes through separate pixels of a spatial light modulator (SLM) or acousto-optic modulator (AOM). For this work, we utilize an SLM, which modifies each spectral component using computer controlled phase and amplitude. When the pulse is spectrally and temporally reconstructed through the second spectrometer, the addition of spectral phase or modulation of amplitude causes the initially short, simple pulse to be more complicated in the time and frequency domains. This process provides a versatile computer controlled time-dependent electric field that can be shaped to control the interaction of the field with molecules, thereby manipulating the molecular dynamics.

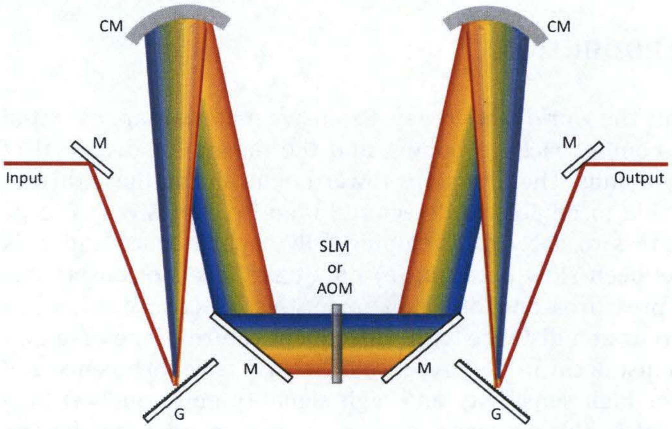

Fig. 1. Schematic diagram of a femtosecond pulse shaper. Colors in the ultrafast laser pulse are separated using a grating and collimating mirror. A mask (either spatial light or acousto-optic modulator) located at the Fourier plane adds phase to and/or modulates the amplitude of each color. The colors are reassembled using a second focusing mirror and grating.

ODD-Ex combines the ability to shape femtosecond optical pulses with advanced machine learning algorithms to quickly determine the pulse shape that optimizes a unique signature for a specific molecule. The concept of using an experimental feedback loop to determine the optimal pulse shape was first proposed by Judson and Rabitz [7], and has since become common practice in a range of applications [8]. For explosives detection, the plan is to first assemble a library of optimal pulse shapes for different types of explosives. This library of optimal shapes may then be scanned at up to kHz rates to rapidly identify any potentially threatening materials. These optimal pulse shapes must be robust to different background materials that may also be present and which would normally overwhelm the signal from the explosive. One of the major advantages of ODD-Ex over conventional laser based detection methods is its ability to shape the pulse in such a way that the laser does not excite signals from interfering materials. Another advantage is the capacity to utilize time-dependent molecular dynamics for discrimination amongst very similar molecules [9]. Of course, the implementation can be performed using a number of different types of spectroscopy. Recent results for one of these implementations, ODD-CARS, are discussed below. We discuss here the application of the Gerchberg-Saxton algorithm to deriving pulse shapes optimized for excitation of coherent anti-Stokes Raman signals from a target analyte in a bath of interfering materials.

2. ODD-CARS

We have focused recently on applying the ODD-Ex paradigm to coherent anti-Stokes Raman spectroscopy, or CARS. The rationale for choosing CARS is that it is a nonlinear form of Raman spectroscopy, which has already proven to be a very good method of detecting and identifying explosive materials. ODD-Ex therefore supplements an already existing laser based spectroscopy to make it even better. The large signals and beam directivity inherent in CARS potentially avoid the problem of fluorescence interference that typically plagues ordinary Raman measurements of colored materials. Experiments of other groups also suggest that femtosecond pulse shaping implementations of CARS show significant promise [10-12]. Using the framework of ODD-Ex to find pulse shapes that optimize CARS signals, we have shown that the explosive signal can be maintained while reducing the signal from interfering materials present by orders of magnitude (See Figure 2) [13]. Significant improvements in selectivity can be achieved in this manner.

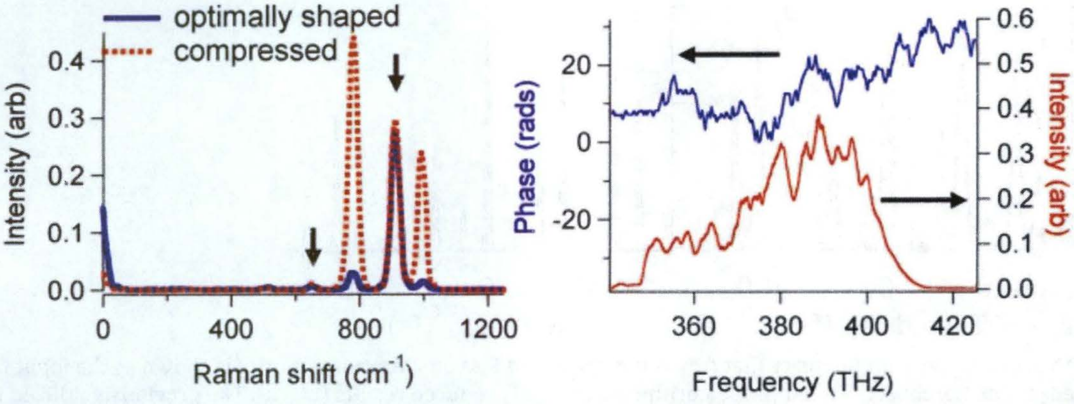

Fig. 2. The CARS spectrum of a mixture containing nitromethane and interfering species is given by the red dashed line. Shaping the pulse as shown in the right panel leads to the CARS spectrum given by the blue line. The nitromethane peaks marked by arrows remain, while the largest interfering peaks are significantly reduced. This is due to selective excitation of the nitromethane, detailed in ref (12). Used with permission.

A significant time is usually needed to determine the optimal pulse shape for these CARS experiments using the standard ODD methodology (closed loop machine learning) even with application of the latest evolutionary strategy optimization algorithms [14]. We have been exploring the ability to more rapidly obtain the pulse shape for a desired analyte CARS spectrum using the Gerchberg-Saxton algorithm to produce a starting phase versus frequency for the SLM mask. The Gerchberg-Saxton algorithm is a common means of phase retrieval in imaging systems. Essentially, source and target intensity distributions related by a Fourier transform are known, and the Gerchberg-Saxton algorithm is an iterative scheme for finding the phase that can best achieve the target intensity distribution from the source. The Gerchberg-Saxton algorithm can also determine the spectral phase required to obtain an arbitrary temporal intensity profile for a given femtosecond laser spectrum, since they are also related by Fourier transform. Therefore, if we can determine the temporal intensity profile that will excite a given Raman spectrum, the Gerchberg-Saxton algorithm can find the spectral phase mask to achieve that intensity profile .We utilize the Gerchberg-Saxton pulse shaping methodology described by Rundquist et al. [15], which requires knowing the target spectrum and the laser spectrum. We determine the spectral phase mask required to excite a given Raman spectrum with the following procedure, the GS algorithm:

1. Tabulate the spectral peak frequencies characteristic of the molecular spontaneous Raman response.
2. Fourier transform from the frequency to the time domain.
3. Keep only the positive amplitude components of the time domain field and limit the corresponding oscillation time to a few picosecond time window.
4. Use the Gerchberg-Saxton algorithm to determine the spectral phase required to maximally match this temporal intensity profile, I(t).
5. Calculate I(t) for the GS optimized pulse.
6. Calculate the two photon difference frequency CARS excitation spectrum for the GS optimized pulse; this is the excitation filter function.

Distinct advantages of this methodology are that the GS algorithm is independent of target complexity and there are no cost functions, weight factors, or parameters to optimize. We have discussed this approach in previous publications [16, 17] and show here recent results obtained in mixtures of interest to the explosives detection community.

In our previous reports [16, 17], we used the GS algorithm to calculate optimal phase masks using the direct Fourier transform of the experimentally measured (Ahura First Defender) analyte Raman spectrum as the intensity target. That process led to observable disagreement between the measured and calculated second harmonic generation (SHG) spectra for the GS optimized pulse shapes. We now replace each peak in the analyte Raman spectrum with a delta function. The process is illustrated in Figure 3.

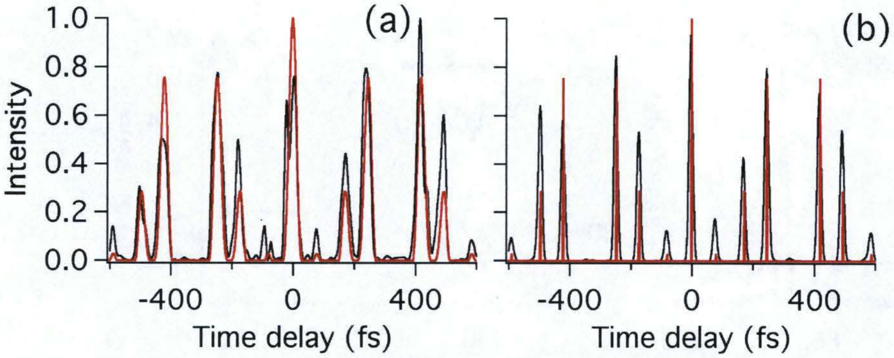

Fig. 3. The time-dependent intensity that drives the optimized Raman vibrational modes is shown as the input target (red) to the Gerchberg-Saxton (GS) algorithm and the GS produced results (black). The previously utilized GS target (a) consists of broad features that are temporally larger than the compressed pulse width. The new GS target (b) replaces each broad peak with a delta function that generates a train of compressed pulses that is easier to produce experimentally. See text for further details.

We also identified some spectral resolution limitations within our pulse shaper. At present, our pulse shaper utilizes a spatial light modulator with 5 mm tall pixels. The current cylindrical focusing mirrors give a diffraction limited spot size with ~ 10% energy leakage onto adjacent SLM pixels. Computer simulations show that this energy leakage affects the GS optimization. To circumvent this inadequacy, we currently bin two adjacent pixels together to allow CARS selectivity, but with somewhat less than the full potential of the GS algorithm. We are in the process of rebuilding the SLM-based pulse shaper to achieve single pixel resolution, and are also implementing the unevenly-spaced Fourier transform (Lomb transform) in the GS algorithm to account for the unevenly spaced frequency steps across the pulse shaper.

2.1 ODD-CARS Experiment

All results given below were obtained using 1 kHz repetition rate, 1 mJ energy, 25 fs pulses from a Coherent Legend Elite Ti:sapphire based ultrafast laser system, with central wavelength near 800 nm. The pulses were spectrally broadened via self-phase modulation in a filament produced by weakly focusing into a 1 m long pipe filled with ~40 kPa of argon gas. The broadened spectrum was passed through an all-reflective pulse shaper, consisting of a 600 l/mm grating, 500 mm focal length cylindrical mirror, turning mirror, 640 pixel dual mask spatial light modulator (Cri 640-D-VN SLM) and retro-reflecting mirror which slightly displaces the output beam in the vertical direction to allow spatial separation of the incoming and outgoing beams. We utilized the multiphoton intrapulse interference phase scan (MIIPS) process [18] to produce nearly transform-limited pulses after the filamentation in argon. The MIIPS phase was saved and added to the GS algorithm-produced phase in all subsequent experiments. Finally, a portion of the original 800 nm pulses was frequency doubled in a 6 mm BBO crystal to generate the narrow band 400 nm used as the CARS probe. All of the pulses were made collinear for application to future standoff experiments in scattering geometry. For the measurements reported here, the focusing lens was 300 mm focal length and a collection lens of 30 mm focal length was positioned at a backscattering angle of ~30 degrees, or collinearly with the focusing lens for transparent materials. Experiments were performed in transmission geometry for transparent materials, and scattering geometry for solids and turbid solutions. The use of a probe pulse spectrally separated from the excitation pulses avoids interference from the femtosecond CARS emission, as has been reported in similar experiments [12].

We utilize a version of CARS based on impulsively stimulated Raman spectroscopy (ISRS) [19]. ISRS uses a spectrally broad excitation pulse such that two electric field interactions excite difference frequencies with the spectral bandwidth of the pulse. Each pair of frequencies with a difference frequency equal to the Raman frequency (ω_1-ω_2=ω_{Raman}) contributes to the excitation as a complex product of the field amplitudes. The integral over all frequencies provides the excitation spectrum. For ODD-CARS, a third spectrally narrow pulse that is delayed in time probes the vibrational free-induction decay (FID) initiated by the first two fields. The interaction of the third field with the FID produces a fourth emitted CARS field as an anti-Stokes modulation of the probe field. This method allows full spectrum acquisition in a single shot without the nonresonant background typical in nanosecond CARS. The nonresonant background disappears when the third pulse does not overlap the first two pulses in time. There is a tradeoff between the spectral resolution defined by the third pulse and the minimum delay time that can be used. A narrower probe spectrum will be longer in time by the uncertainty principle and will require a longer time delay to avoid pulse overlap. Since the coherent signals are decaying with time we have chosen a moderate spectral resolution and < 1 ps probe pulsewidth.

For the results shown below, 0.5 s integration times were used. GS optimizations were performed with a 2 ps total time window. Pulse energies were typically set to the maximum signal to noise for compressed pulses without generating competing nonlinear supercontinuum signals, which are damaging to the sample, typically ~10 μJ. The 400 nm probe pulse was typically delayed by 2 ps to ensure it was temporally separated from the shaped pulse train. A background subtraction was performed with the excitation pulses blocked. When comparing compressed and optimized pulses, nothing was changed except the mask on the SLM; the sample was not moved, the energy was not changed, and no optics were adjusted. The comparisons here are primarily relative between unshaped and shaped pulse CARS under identical conditions, except as noted.

2.2 ODD-CARS Results

We obtained ODD-CARS for nitromethane as the target analyte in a mixture composed of 2 parts nitromethane, 2 parts cis-stilbene, 1 part acetone and 1 part toluene, by volume. The results are shown in Figure 4, which nicely illustrates the primary effect of pulse shaping on CARS spectra. The peaks marked by asterisks are the nitromethane peaks, which are optimized for excitation in Figure 4b and 4c. Figure 4a is a compressed pulse, non-optimized, CARS spectrum of the mixture. Clearly, the peak intensities have all decreased in Figure 4b, but more so for the interfering peaks. This is a typical result for a three-peak optimization at the same laser energy. The quantum interference effects are more constructive for the optimized peaks than for the interfering peaks. All peaks diminish due to the lowered laser intensity, since a 20 μJ 10 fs pulse has much higher intensity than a 20 μJ 2 ps pulse train.

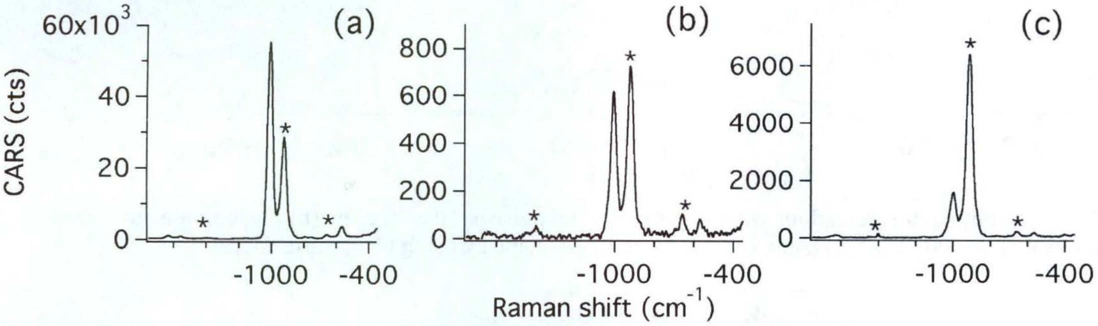

Fig. 4. CARS of 33% nitromethane, 33% cis-stilbene, 16.7% toluene, and 16.7% acetone at 2 ps probe delay. Asterisks mark nitromethane peaks. a) compressed pulse CARS at 20 μJ; b) GS optimized CARS at 20 μJ; c) GS optimized CARS at 140 μJ.

We also investigated nitromethane in a mixture with gasoline. The gasoline had a prominent CARS signal as well as some broad emissions, which were diminished using GS optimization of the nitromethane excitation as shown in Figure 5, similarly to what was observed for nitromethane in the toluene/stilbene/acetone solution of Figure 4. Here the signal to noise using the optimal pulse at 20μJ energy is significantly decreased relative to the compressed pulse. Increasing the pulse energy for the shaped pulse allows the signal to noise to be increased, as shown in Fig. 5c. Shaping the pulse allowed more energy to be used on the sample (longer total pulse length implies lower laser intensity), increasing the total emission while selecting for the nitromethane CARS emissions.

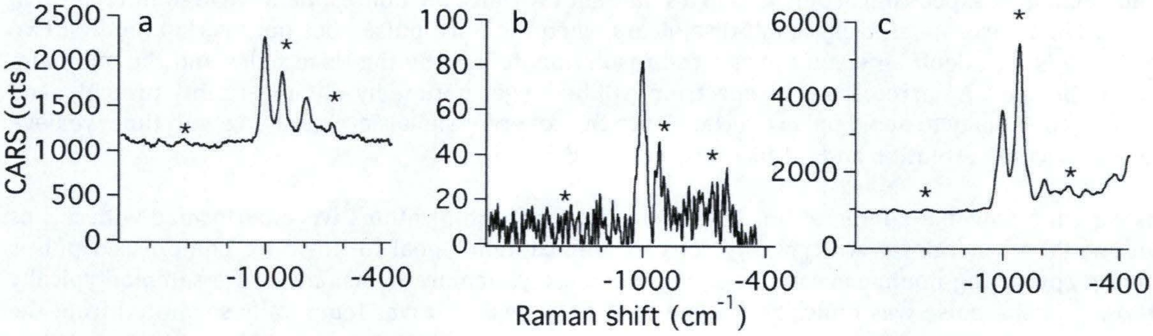

Fig. 5. CARS of 50% nitromethane in gasoline. Asterisks mark the nitromethane peaks. The compressed pulse (a) shows the CARS of the mixture at 20 μJ pulse energy, which is optimized in (b) for nitromethane, also at 20 μJ pulse energy. Increasing the energy to 140 μJ recovers the CARS spectrum with enhanced nitromethane peaks relative to the inferences.

We also investigated several powder mixtures. An example is given in Figure 6, for ammonium nitrate in a 10% mixture in flour. The materials were ground using a mortar and pestle, but were still inhomogeneous so that the signal levels varied significantly with spatial location. Figure 6 compares relative signals at the same location for a compressed pulse and a pulse optimized using the GS algorithm for ammonium nitrate. Note that optimizing on the single strong 1040 cm^{-1} AN peak did not lead to any loss of signal even at the same energy as the compressed pulse (compare Figure 6 a and b).

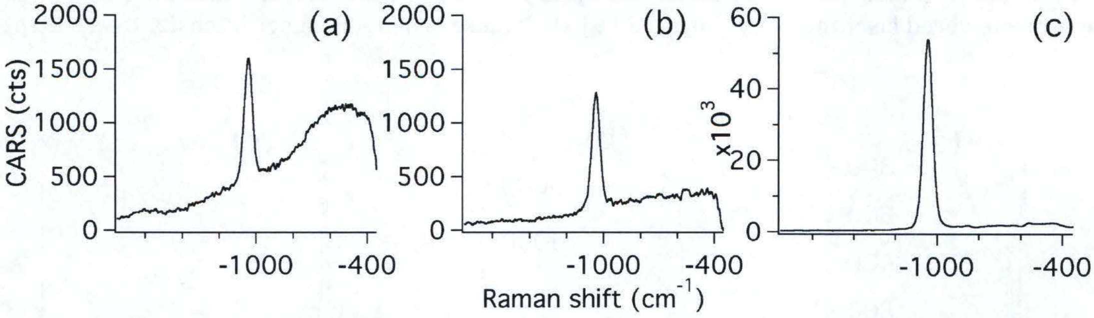

Fig. 6. CARS of 10% ammonium nitrate in flour with: (a) compressed pulse of 20 μJ energy; (b) pulse shape optimized for ammonium nitrate (also 20 μJ energy); and (c) optimized pulse shape by using 65 μJ pulse energy.

4. OUTLOOK

There are a number of scientific problems yet to be solved in order to successfully exploit pulse shaping methodologies for explosive detection and multiple research groups around the world are working to address these problems. Continued work is needed to better understand and predict the interactions between shaped laser pulses and complex molecular species and complex backgrounds or mixtures. High fidelity control relies upon improvements in laser source spectral bandwidth, pulse to pulse stability, and the ability to deliver properly shaped pulses at a distance through turbulent and dusty air. We are pursuing these goals using complementary tools, exploring a variety of nonlinear spectroscopies and optimization methods. ODD-CARS using the Gerchberg-Saxton algorithm is capable of providing selectivity for a target analyte in mixtures, applicable to scenarios including analytes on backgrounds or in matrices. Other complementary methods to exploit the capabilities of ODD-Ex to distinguish between very similar molecules are also being investigated.

ACKNOWLEDGEMENTS

We are grateful for support from the Office of Naval Research and the US Department of Homeland Security. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the US Department of Energy under contract DE-AC52-06NA25396.

This paper has been released as LA-UR 12-XXXXX.

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