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Optimal Dynamic Detection of Explosives

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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 standoff 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 complementary ODD-Ex methods.

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 stand-off 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 detect 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 a few 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 can 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 at a maturation level sufficient to attack applied problems such as explosive detection.

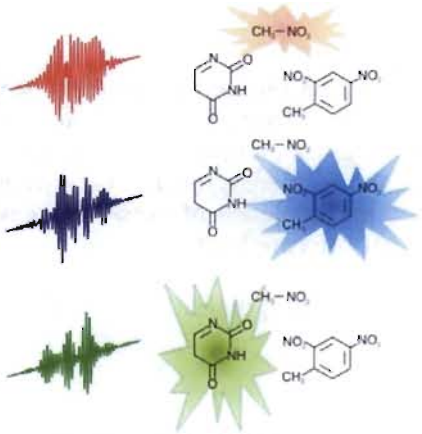

Fig. 1. The basis of Optimal Dynamic Detection of Explosives (ODD-Ex) relies on the ability to send a shaped laser pulse into an ensemble of molecules that selectively produces a detectable signal only from the chosen type of molecule.

The technological basis for shaping femtosecond laser pulses utilizes a programmable phase and amplitude mask located in the Fourier plane of a zero dispersion stretcher [5,6]. A zero dispersion stretcher is in essence a subtractive double spectrometer with the mask placed at the central focal plane. At the mask, the colors are spatially separated and each spectral component interacts with separate pixels of a spatial light modulator (SLM) or acousto-optic modulator (AOM). The SLM modifies each spectral component using a 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.

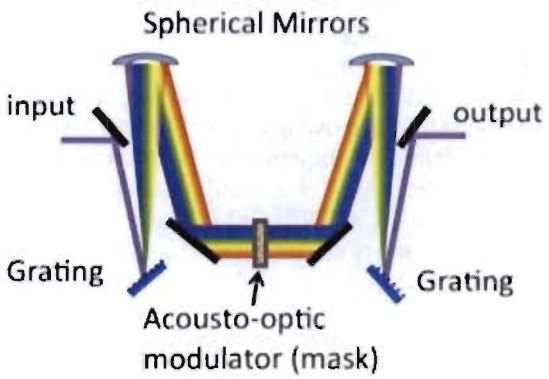

Fig. 2. Schematic diagram of a femtosecond pulse shaper. Colors in the ultrafast laser pulse are separated using a grating and collimating mirror. An mask (either spatial light or acousto-optic modulator) located at the Fourier plane adds phase to and/or modulates the amplitude of each color. The colors 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 idea 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 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 will not excite 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 two of these implementations are discussed below.

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 to 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 [10,11]. 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 [12]. Significant improvements in selectivity can be achieved in this manner.

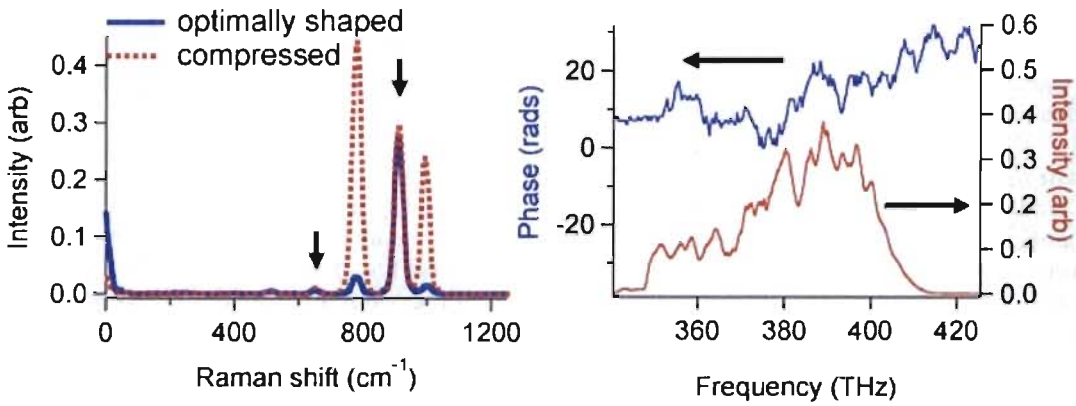

Fig. 2. The CARS spectrum of a mixture containing nitromethane and interfering species is given by the red dashed line. Shaping the pulse as shown in the right panel leads to the CARS spectrum given by the blue line. The nitromethane peaks marked by arrows remain, while the largest interfering peaks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

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. 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. In full optimizations where the analyte is unknown (e.g., the target is an uncharacterized mixture of materials or a vapor scent of unknown composition), evolutionary strategies of various kinds (e.g., genetic algorithm or GA) are necessary to find the optimal phase mask, but the process can be slow. However, for scenarios where the analyte is a known material (i.e., a given explosive), the Gerchberg-Saxton algorithm provides a very fast method to produce the phase mask for that particular analyte. We utilize the Gerchberg-Saxton pulse shaping methodology described by Rundquist et al. [13], which requires knowing the target spectrum and the laser spectrum. We assume that the two photon excitation spectrum is equivalent to the target spectrum, which is approximately true for CARS spectra with no electronic resonances. 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.

The GS algorithm begins with a fast Fourier transform (FFT) of the experimentally measured pulse (laser) spectrum assuming random phase in the time domain. The amplitude is then replaced with the target spectrum while retaining the phase (the target is initially set as the IFFT of the spontaneous Raman spectrum of the analyte). An IFFT is then performed to transform back to the spectral domain, where the amplitude is replaced with the input pulse spectrum and the phase is again retained without change. The process is iterated many times, until there are only small residual changes in the retained phase. On the last iteration, the retained phase is the desired phase mask optimized for the analyte.

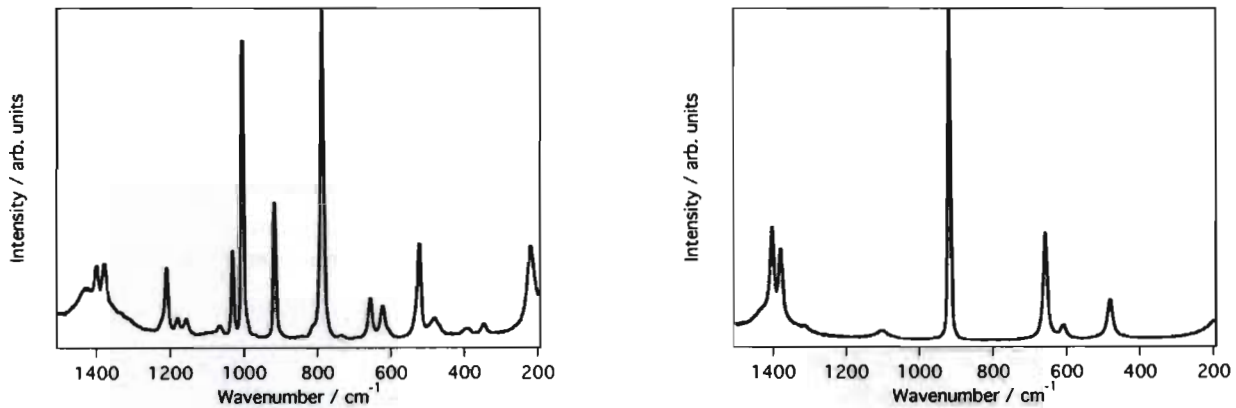

Fig. 4. Left –Raman spectrum of a mixture of interferences (acetone and toluene) plus nitromethane as the target analyte; Right –Nitromethane Raman spectrum as the target spectrum for the GS algorithm.

To demonstrate the GS capability in a series of computer simulations, we compared GA and GS algorithms in their ability to find a spectral phase that extracted a target spectrum (Figure 4 right – the Raman spectrum of nitromethane) from a mixture CARS spectrum (Figure 4 left) with many interfering peaks. The GS algorithm was able to produce a reasonable suppression of the interfering peaks and a reasonable facsimile of the NM CARS spectrum after only 10 seconds (1500 iterations), starting from the NM Raman spectrum as the input. See Figure 5 below (final spectral phase on the left and CARS spectrum – equivalent to the two-photon excitation spectrum – on the right). This simulation would be a perfect fit to the target spectrum without the limitations intentionally imposed to mimic experimental conditions, i.e., limited spectral resolution, limited number of SLM pixels, defined dephasing time, and limited laser bandwidth (simulation used a 10 fs FWHM Gaussian laser pulse).

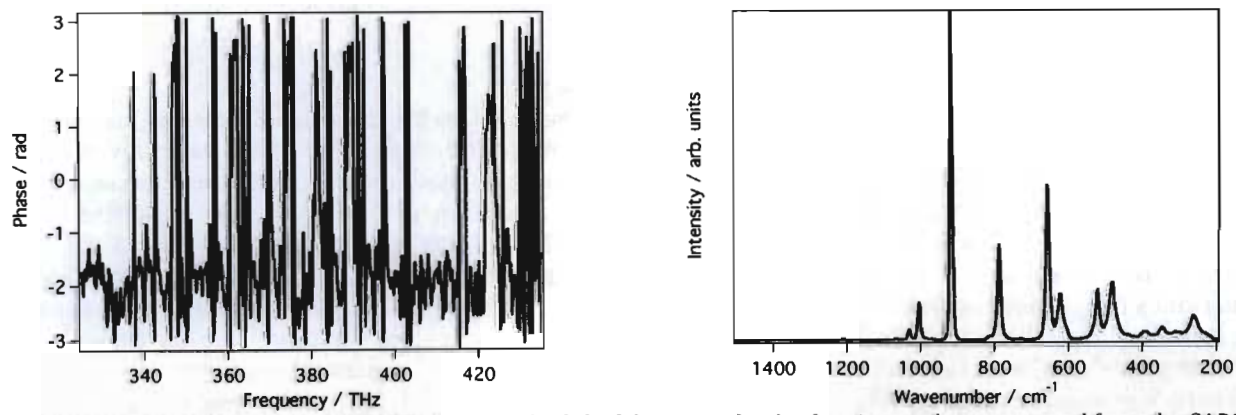

Fig. 5. Spectral phase (left) and CARS spectrum (right) of the optimal pulse for nitromethane extracted from the CARS spectrum of the mixture shown in Figure 4 (left side) after using the GS algorithm (simulation results). The incomplete suppression of the non-nitromethane peaks is partly due to non-zero Raman intensity between the peaks in Figure 4 and partly due to the reasons discussed in the text above.

To experimentally demonstrate the capability of the GS algorithm to provide a reasonable pulse shape for a target material, we used a mixture of NM, toluene, and acetone (1:2:2 by volume). The Raman spectra of neat nitromethane and the NM/toluene/acetone 1:2:2 mixture are shown in Figure 6. Figure 6 also shows the two photon excitation spectrum from the GS algorithm compared to the nitromethane Raman spectrum (right hand side).

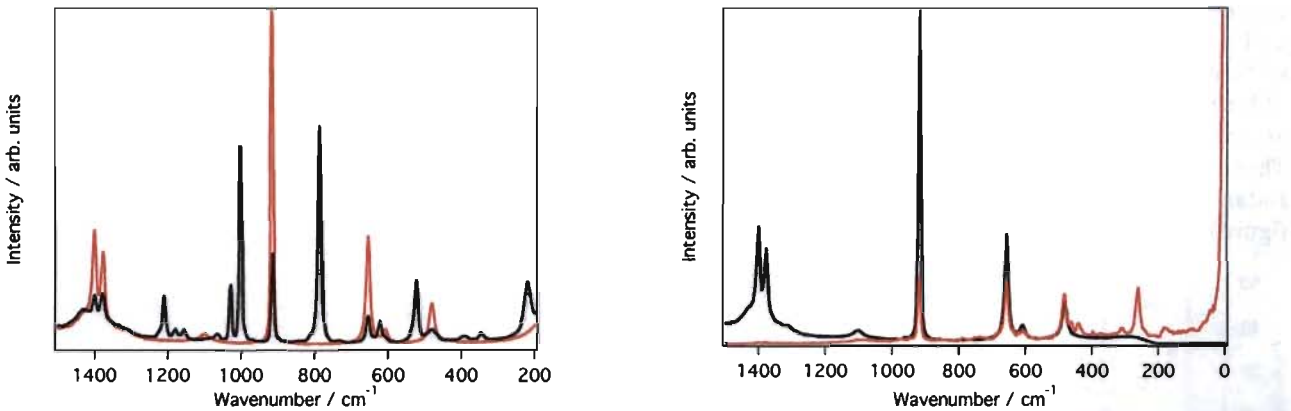

Fig. 6. Left – Raman spectra of nitromethane (red curve) and the 1:2:2 mixture of nitromethane/toluene/acetone. Right – Two-photon excitation spectrum (red curve) resulting from the GS algorithm using the nitromethane Raman spectrum (black curve) as the target. The spectral phase giving rise to this two-photon excitation spectrum is shown in the right side of Figure 7 below.

The results from use of the GS algorithm to derive a shaped pulse specific for nitromethane are illustrated in Figure 7. The black curve shows the CARS spectrum of the mixture using the compressed (transform limited) pulse. The GS algorithm was then used to obtain the spectral phase optimized for nitromethane by using the nitromethane Raman spectrum as the target. This spectral phase was then used to produce a CARS spectrum from the mixture (red curve), showing significant enhancement of the nitromethane vibrational features over those of the other mixture components. Compare this result with that shown in Figure 3 above, realizing that the optimization took 10 seconds for the GS algorithm, versus 12 hours for the GA result.

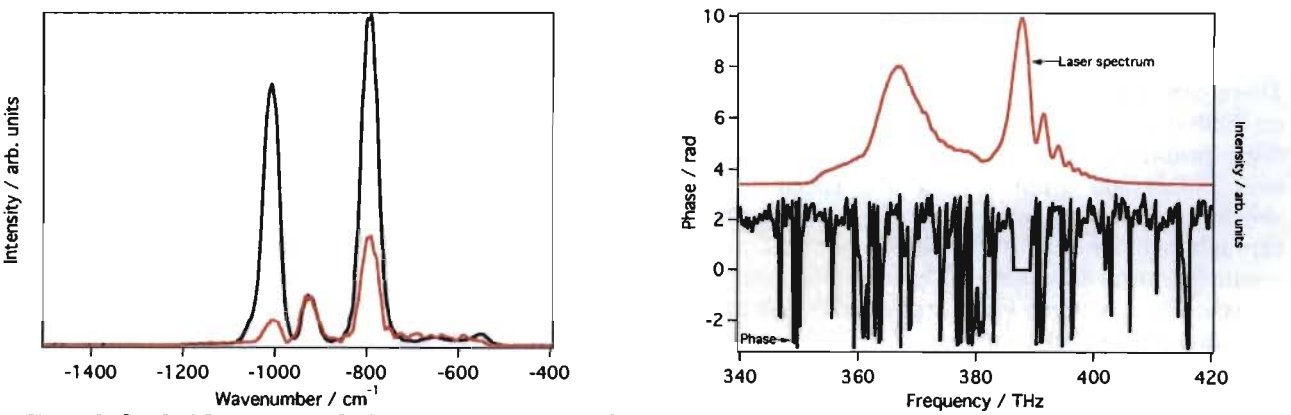

Fig. 7. Left – CARS spectrum of toluene:acetone:nitromethane mixture (2:2:1 by volume) using the compressed pulse (black curve) and the spectral phase shown at right (red curve). The nitromethane feature at 917 cm^{-1} is significantly increased relative to the toluene and acetone peaks using the GS derived spectral phase. Right – The spectral phase (black curve) which is the result of the GS algorithm using the nitromethane Raman spectrum as the target. Also shown is the laser spectrum used in the experiment (red curve).

3. EXPLORING THE FUNDAMENTAL LIMITS OF ODD-EX

The work at Princeton has focused on exploring the fundamental chemical selectivity limits of ODD and extending its general applicability for domains that include atmospheric investigation, biological discrimination, and rapid molecular interrogation. For instance, shaped pulses are able to evince disparate dynamical responses from two complex biological molecules indistinguishable via their linear absorption and fluorescence spectra [9]. This capacity for creating distinguishing excitations among nearly identical molecules is also critically exploited for the ODD-Ex paradigm. One approach undertaken by the Princeton team has utilized shaped femtosecond pulses to selectively ionize a target material in the vapor phase while minimizing indiscriminate or deleterious ionization of background interferents. The resultant laser-induced plasma then scatters high frequency microwaves, which are coherently detected with established homodyne techniques for excellent long range detection possibilities. This unique combination of specificity afforded through optical pulse shaping and high detection sensitivity from radar scattering has yielded dramatic improvements in ionization selectivity compared to unshaped pulses (see figure), and further advances are expected with continued experimentation.

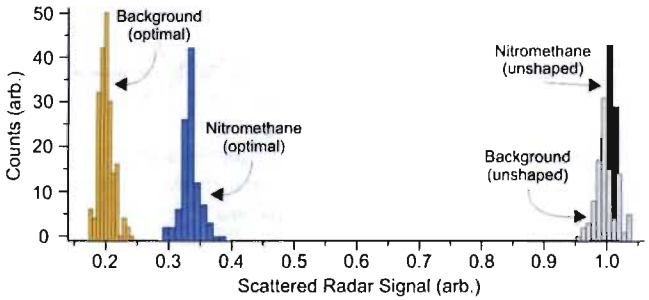

Fig. 7. In the absence of pulse shaping, the ionization probability of nitromethane (black) and a background interferent (gray) are indistinguishable, which thereby precludes meaningful discrimination. With a properly shaped pulse form, however, the ionization probabilities for nitromethane (blue) and the background (gold) become resolvable. Subsequent radar scattering from this optimally controlled plasma now permits statistically significant discrimination.

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. 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 by the two groups involved in this collaboration.

ACKNOWLEDGEMENTS

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