

Femtosecond pulse shaping adds a new dimension to mass spectrometry

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Phase-shaped femtosecond laser pulses and mass spectrometry were implemented as a tool for improving molecular identification. We demonstrate that the specific lines in the mass spectra of several chemical warfare simulants are sensitive to the phase characteristics of the incident laser field. The deviation in the relative yield of fragment ions observed upon pulse shaping (enhancement or suppression) adds a new dimension to mass spectrometry that improves molecular identification and can be used to quantitatively analyze mixtures of isomers. © 2007 Optical Society of America

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1. Introduction

Detection and identification of chemical species in real time is of significant importance for both environmental and security applications. Mass spectrometry (MS) is widely used for air quality monitoring, usually boosting its reliability by increasing the multidimensionality of the analysis. Compact, portable, backpack-sized MS devices [1] are commercially available, although still not providing zero false positives that are a prerogative in critical applications. Traditionally higher reliability and/or confidence level (increased dimensionality of analysis) has been achieved by adding gas chromatography (GC) or another MS in the analytical path, therefore providing two- (GC-MS) or three- (GC-MS-MS) dimensional analysis [2]. This approach increases the reliability of results (low false positives) but inevitably increases the response and/or analysis time to several minutes.

It has been established that shaped femtosecond pulses can influence the relative yield of fragment ions [3–6]. We report here on significant advances in fast photonic identification of chemicals based on binary shaped [7] femtosecond pulses. The method presented here combines a femtosecond laser with a

phase shaping module and a time-of-flight mass spectrometer [5]. The advantage of the system is that the laser-molecule interactions depend on the pulse characteristics and the electronic and molecular structure of the analyte. This dependence is reduced to a parameter given by $\delta \equiv \langle Y - Y_{TL} \rangle$, which determines the average deviation for each fragment ion from a reference, which we have chosen to be the relative yield of that fragment obtained for transform-limited (TL) pulses.

Previous work from our group focused on singular differences in the mass spectra resulting from the application of differently shaped ultrashort fields [5]. The new approach presented here emphasizes the observed deviation δ (enhancement or suppression) in the yield of particular fragment ion peaks as a result of pulse shaping. Therefore we utilize not only the position and intensity of MS lines for identification, but also an average deviation for each spectral line upon pulse shaping. Here we present this new approach of multidimensional mass spectrometry for real-time analysis of warfare agent analogs.

2. Experimental Section

Experiments were performed using regeneratively amplified femtosecond pulses, with 35 fs pulse duration, full width at half-maximum, produced by a commercial Ti:Al₂O₃ laser system as described in Ref. 5.

Phase distortions were measured and eliminated to obtain TL pulses by using the self-calibrating multiphoton intrapulse interference phase scan (MIIPS) method [8]. Having TL pulses is a crucial step in this approach, as the MS obtained from TL pulse serves as an internal standard; furthermore, it ensures the reproducibility of the results. Femtosecond lasers, unlike nanosecond and picosecond sources, are prone to phase distortions, which cause temporal broadening. This is why we stress the importance of correcting spectral phase distortions at the location where the laser interacts with the molecules. MIIPS ensures that phase distortions inherent to the laser system, as well as distortions introduced by the optics in the beam path, are all eliminated. With MIIPS, obtaining TL pulses at the sample takes only 20 s. MIIPS uses a pulse shaper with a liquid-crystal-based spatial light modulator that is situated between the oscillator and the amplifier. The measurement of spectral phase distortions is accomplished by introducing a reference phase function. Once phase distortions are measured, they are compensated by the pulse shaper, thus obtaining TL pulses. This setup preserves the total output power of the laser and produces accurate spectral phase modulation [9].

The new dimension introduced in this work depends on causing significant and reproducible changes in the fragmentation pattern of molecules when studied by mass spectrometry. Pulse shapers use spatial light modulators to control the phase and amplitude of different frequency components of the pulse. The shaper used for this work has 128 pixels, and each can introduce 100 different phases and 100 amplitude levels. The total number of different shaped pulses that can be generated is $(100 \times 100)^{128} = 10^{512}$. In the same laboratory, we have pulse shapers with 640 pixels, which can generate 10^{2560} different-shaped pulses. These numbers are well beyond astronomic proportions. In fact, the number of atoms in the universe is estimated at 10^{80} . Clearly, in order to create a useful application, the task is to reduce the number of shaped pulses that need to be evaluated to the absolute minimum and to be certain that those shaped pulses can be reproduced by every laser used for molecular identification. During the past 3 years, we have been working on exploring the minimum number of phases required for molecular identification. The greatest reductions have resulted from two observations. First, amplitude modulation is similar to pulse attenuation, and we have found that pulse attenuation causes minimal changes to the fragmentation pattern. Furthermore, because multiphoton pulses depend on the relative phase of the different frequency components in a femtosecond pulse, we can control their amplitude with phase-only modulation [7]. Second, we have realized that by using binary phase changes, we can cause maximum changes to the pulses and minimize redundancies. Binary phase modulation also gives us extremely high reproducibility, as enjoyed in digital

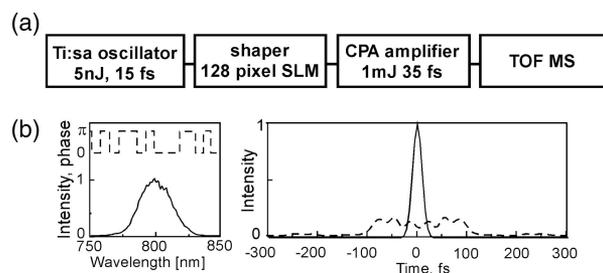


Fig. 1. (a) Schematic experimental setup used for these experiments. Commercial 15 fs oscillator output is directed through the LC-(Cambridge Research and Instrumentation, Model SLM128 D VN) based pulse shaper in the folded $4f$ configuration, where $f = 150$ mm. Dispersion element is a gold diffraction grating with 830 grooves/mm (Edmund Optics). Shaped pulses are directed through the standard commercial chirped-pulse amplifier. A base pressure of 10^{-7} Torr is maintained in the time-of-flight mass spectrometer by a three-stage differential pumping scheme with a mechanical roughing pump, a diffusion pump, and a turbo pump. The sample is effused to the chamber by an inlet valve up to a pressure of 10^{-5} Torr for experiments. The spectrum of the laser pulse is shown in (b) together with a typical binary phase. The femtosecond laser pulse is also shown in the time domain when it is transform limited (solid curves) and when it is shaped (dotted curve).

electronics. Based on these general principles, we proceed to show results using 8 bit binary-shaped pulses.

Femtosecond pulses have a broad bandwidth, which was divided in eight bins where the phase in each bin can be set to 0 or π , allowing 256 different phase shapes. To determine δ , a sequence of 256 binary phase-shaped (BPS) pulses interacts consecutively with the sample and time-of-flight mass spectra are recorded for each implemented binary phase shape. From these measurements, we calculate δ . A schematic of the experimental setup is presented in Fig. 1(a). The spectrum of the pulse is not affected by spectral phase modulation, and a sample binary phase of the shaped pulse is presented in Fig. 1(b) in the left panel. The temporal profile of the TL and a binary-shaped pulse are presented in the right panel of Fig. 1(b). For real-time applications, only TL and one shaped pulse are required to obtain a mass spectrum and δ , making molecular identification possible in a subsecond time scale.

For a given BPS pulse, 128 mass spectra are collected and averaged. The standard deviation from each such average is $<5\%$. The laser system has a 1 kHz repetition rate, which allows us to evaluate 256 different BPS pulses in a few minutes. The entire set of measurements has some redundancies built in that we use as internal control experiments. The 256 BPS pulses have a $2\times$ redundancy because addition of π across the spectrum leads to identical pulses. We look at this symmetry to make sure that the shaper and the laser system are performing as expected. Once a particular molecular system is characterized, there is no longer a need for running 256 different BPS pulses. By comparing changes between TL and a single BPS pulse, we gain sufficient information to identify compounds apart, provided that they have been characterized before.

The results presented here were obtained by focusing 150 μJ pulses using a 50 mm focal length lens. The sample was introduced effusively up to a background pressure of 10^{-5} Torr under fast flow conditions. Laser-induced ionization took place between the repeller and extractor plates of the time-of-flight mass spectrometer. We arrived at these conditions after experimenting with every parameter in the setup. We tested $>10^4$ different phase-shaped pulses, and evaluated different pulse intensities and pressures. The complete set of experiments is now compiled for publication elsewhere [10], and it is beyond the scope of this paper. For this research, the peak power density of TL pulses was $\sim 10^{16}$ W/cm². Changes in the laser pulse energy from 20 to 200 μJ made no difference on the observed results [10]. Similarly, small changes (~ 20 nm) in the excitation wavelength make no difference on the observed results. However, phase changes that lead to longer pulses, such as chirp, sinusoidal modulation, and binary phase modulations, have a similar effect in that they reduce the total number of ions detected. Typically, TL pulses favor larger fragment ions, while heavily phase-shaped pulses favor smaller fragment ions.

3. Results

As a consequence of the nonlinear dependence of ionization and fragmentation resulting from laser-molecule interactions, the integrated intensity of the mass spectrum decreases from a maximum obtained for TL pulses to lower values obtained with phase-modulated pulses [11,12]. By normalizing the mass spectrum obtained for each shaped laser pulse, it is possible to determine the relative yield of each fragment ion given a particular shaped pulse. The deviation of the average relative yield from the value observed at TL excitation was recorded for each compound. Molecular identification, typically based on the position and intensity of the traditional MS, can now be aided by a new dimension given by the average deviation δ recorded for shaped pulses as illustrated below.

We applied this new strategy to a number of molecules. In Fig. 2 we show the experimental mass spectra recorded using TL pulses for acetophenone, dimethyl phosphite, and phenylethanol. In addition to the MS obtained with TL pulses, we plot the average deviation δ (filled spectrum curve in Fig. 2). Note that some curves show a strongly negative dependence (suppression) on pulse shaping, while others show strongly positive dependence (enhancement). Here we have not evaluated δ for particular pulse shapes; we opted to take the average for a large number of shaped pulses. This makes this new dimension more robust and insensitive to noise. It also allows very fast measurements, requiring less than 0.1 s for molecular recognition.

The application of shaped pulses for detection of chemicals is advantageous when a conventional MS cannot make a positive identification or distinction,

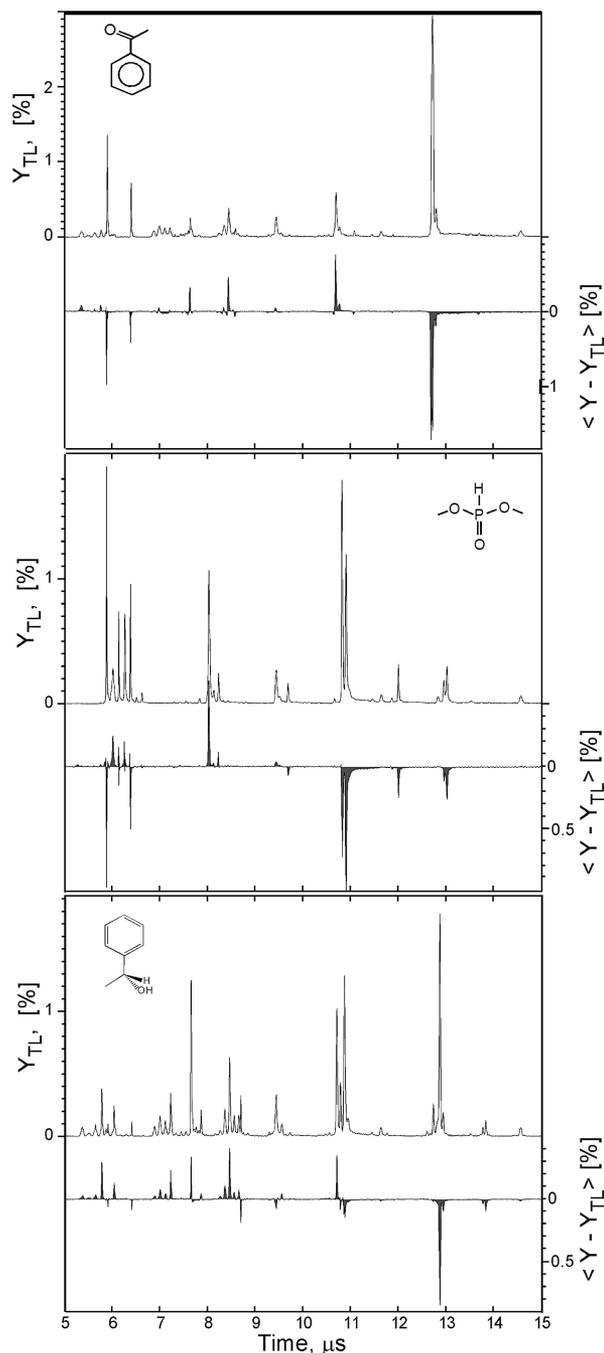


Fig. 2. Mass spectra of acetophenone, dimethyl phosphite, and phenylethanol obtained using TL 35 fs pulses (curves, Y_{TL}). The plot includes the average deviation δ of the mass spectra (filled areas, $\langle Y - Y_{TL} \rangle$) observed upon shaping. The sign and magnitude of δ can be used as an additional dimension, together with m/z and the intensity ratio for real-time molecular identification.

namely, if the sample consists of a mixture of compounds with extensive fragment ion overlaps [13]. Maximum overlap occurs when isomers are present. Isomer identification is typically carried out by the use of special GC columns, and requires several minutes. In Fig. 3 we demonstrate how obtaining δ can help in the identification of *meta*- and *para*-isomers of nitrotoluene. The *ortho*-isomer has a very distinct

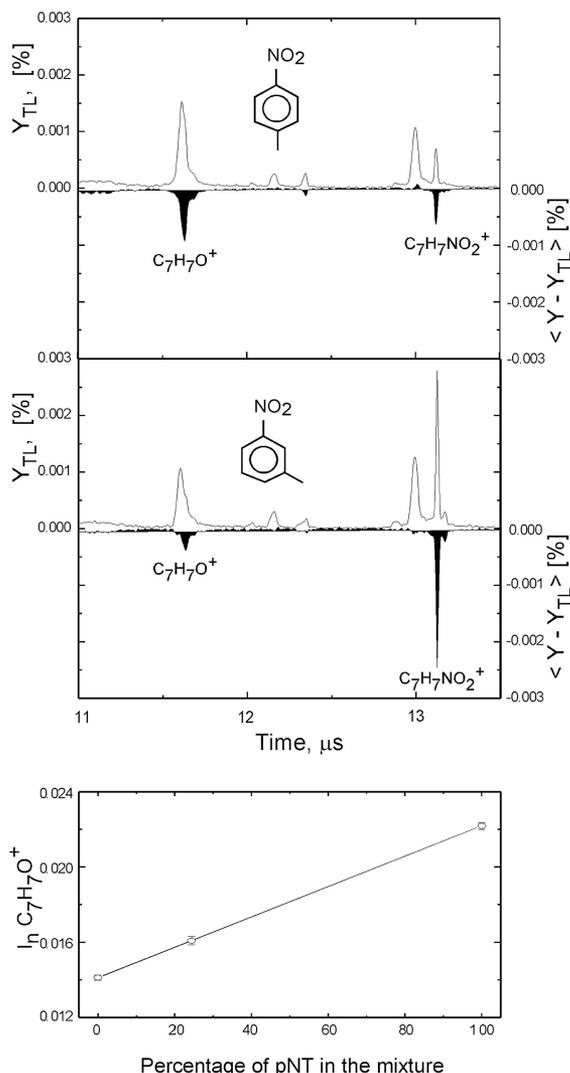


Fig. 3. Portion ($m/z > 100$) of the mass spectra of *meta*- and *para*-nitrotoluene obtained using TL 35 fs pulses (curves, Y_{TL}) with the average deviation δ of the mass spectra (filled areas $\langle Y - Y_{TL} \rangle$) observed upon shaping (top two panels). The magnitude of δ can be used as an additional dimension together with m/z for real-time molecular identification. Quantitative analysis of an isomer mixture (bottom panel). I_n is the integrated value for δ for m/z 107. The three points in the graph represent pure *meta*-, pure *para*-nitrotoluene, and a mixture, prepared to be 23.9% by weight of *para*-nitrotoluene in *meta*-nitrotoluene.

peak that results from a reaction between an oxygen in the nitro group and a hydrogen in the methyl group; therefore, it presents a very different mass spectrum that does not require shaped pulses for identification. The mass spectra of *meta*- and *para*-nitrotoluene isomers under TL excitation are practically identical, with the exception of the peak at m/z of 107 (11.6 μ s) and parent ion m/z 137 (13.1 μ s), which has a difference outside the standard deviation of the measurements. When phase-modulated pulses are applied, each of the isomers yields a small but distinctive δ signature. The sign of δ is negative at m/z 107 for both isomers but four times larger for the *para*-isomer, which is sufficient to separate *meta*-

from *para*-nitrotoluene isomers thus introducing an additional dimension of analysis and boosting the confidence in real-time molecular identification (Fig. 3, top two panels).

Claims for the use of this strategy for isomer identification in mixtures are based on previous experiments from our group where TL and BPS pulses were used to measure the percentage of *ortho*- and *para*-xylene in mixtures [6,13]. To illustrate this point, we performed a measurement on a mixture of *para*-nitrotoluene and *meta*-nitrotoluene and compared it with pure isomers's δ values (see Fig. 3, bottom panel). The mixture contained 23.9% by weight *para*-nitrotoluene. The retrieved concentration from our measurement was 24.4%. This makes us confident that similar mixture analysis, such as that carried out by our group earlier [6,13], would benefit from the δ measurements proposed here.

4. Discussion and Conclusions

The observed results take advantage of the additional fragmentation that is observed for phase-shaped pulses. Based on our extensive studies with different pulse-shaping methods [10], there are many different approaches to introduce phase modulation that would result in similar results. Some may argue that there may be no need for a pulse shaper. Given that the difference used as the new dimension for analysis, introduced here, comes from the difference of a TL pulse and a phase-shaped pulse, it is important to be able to generate a TL pulse. Presently, there are six or more companies offering amplified laser pulses with a bandwidth that supports 35 fs pulses. However, no laser company promises a TL output without the addition of a pulse shaper for pulse compression. Once the laser pulses have transmitted and reflected through a number of optics and arrived at the sample, they have acquired significant phase distortions, and will therefore produce different levels of fragmentation. We argue here that it is critical to make sure that all the phase distortions are eliminated where the laser interacts with the molecules. Only by performing at-the-sample phase correction can one reproduce the experiments presented here. Furthermore, at-the-sample phase correction will be needed in order to produce commercial units that produce identical results when presented with identical chemical mixtures. A pulse shaper with MIIPS is now available commercially from Coherent, Santa Clara, California.

The use of binary phase-shaped pulses for controlled fragmentation and ionization introduces an additional dimension of analysis. Phase-shaped femtosecond pulses and mass spectrometry were implemented as a tool for identification of chemicals, including stereoisomers. A new statistical value that measures the degree to which fragment ions respond to pulse shaping, δ , is used to achieve an important step toward real-time zero false positive molecular recognition with mass spectrometry. We have illustrated isomer identification and the quantitative analysis of a mixture of two isomers.

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