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Systematic chemical recognition using shaped laser pulses

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The paper reports on recent progress towards systematic chemical recognition using shaped femtosecond laser pulses. The ability to generate highly accurate phase functions in which retardation is limited to two values, 0 and π , allows one to carry out an exhaustive evaluation of a 10-bit binary function set in minutes. Upon mining the resulting mass spectra, shaped pulses are found that can be used to uniquely identify a molecule (including structural isomers and stereoisomers) by the resulting fragmentation and ionization pattern. This approach is described and its successful application demonstrated.

1. Introduction

Significant developments have been made over recent years in exploiting the quantum characteristics of light and matter to control the dynamics of atomic and molecular systems. This growth reflects a convergence of factors including the expansion of quantum mechanics as a tool for chemistry and physics, the development of new laser devices which improve the ability to manipulate light, and the recognition that coherent laser light can be used to imprint information on atoms and molecules for practical purposes. Among the potentially relevant applications of coherent laser control is its feasibility as an alternative to standard analytical techniques for chemical identification. Mass spectrometry (MS) is one of the most powerful techniques used today for qualitative analysis of organic and organometallic materials. It is essentially the only technique available for identification of trace chemicals at parts per billion or less. However, structural and geometric isomers are often difficult to distinguish by MS. In addition, quantitative analysis by MS is also quite difficult; usually quantitative determinations are done with gas or liquid chromatography.

Our group has been active in the area of coherent control of nonlinear optical processes, where we have developed the concept of multiphoton intrapulse

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interference, a physics and number-theory based methodology which guides us in the design of phase-shaped laser pulses to optimize multiphoton processes at desired frequencies while minimizing these processes at all other frequencies [1–5]. More recently, we have applied this approach to the molecular recognition of volatile samples [6, 7]. The pioneering work of the Gerber group, which showed that phase and amplitude shaped laser pulses could influence the fragmentation and ionization of molecules [8], inspired us to develop a method that would use specific laser pulses for molecular identification.

Given that laser–molecule interactions depend intimately on the electronic and molecular structure of the analyte as well as on the laser pulse characteristics, it is conceptually possible to find a set of shaped laser pulses that induce uniquely identifying mass spectral fragmentation patterns when they interact with the target analyte. An instrument based on this principle would then use such a set of pulses to provide molecular identification with no false positive/negative results. The challenge, however, is finding the set of shaped laser pulses to be used for identification. This is where our understanding of multiphoton intrapulse interference has provided us with an extremely efficient approach to pulse selection that is based on binary phase functions [4]. The method we have developed is capable of evaluating complete sets of phase functions in a matter of minutes. The results from exhaustive phase evaluation are mined for pulses that show a consistent ability to produce uniquely identifying fragmentation and ionization patterns for molecular recognition. Once this process is complete the system can be used to detect and identify the specified chemical in a sub-second timescale, without the need for additional optimization.

2. Experimental

Our approach to chemical identification with shaped laser pulses is presented in figure 1. The laser pulses, which are generated from a commercially available sub-40 fs 0.8 mJ/pulse amplified laser system with a 1 kHz repetition rate, are first directed to a pulse shaper which is programmed for accurate measurement of pulses and delivery of phase. The femtosecond laser pulses are characterized and spectral phase distortions corrected using multiphoton intrapulse interference phase scan (MIIPS) [3, 9, 10]. With MIIPS we generate transform-limited pulses at the sample, a most important step for achieving reproducible results. After spectral phase correction, a series of binary phase functions, where phase retardation in the pulse shaper is limited to two values 0 and π , are then introduced. The binary phase shaped pulses then interact with the sample, inducing ionization and fragmentation processes. The molecular and fragment ions formed are detected by a time-of-flight mass spectrometer. Typically, the phase functions evaluated correspond to a set of 10-bit binary phases (10 groups of 10 pixels each), which we have found to be sufficient for molecular recognition. The resulting mass spectra for a complete set of phases (1024 measurements) are then mined to construct a subset library which can be used for sample identification. The binary phases are referred to in the text as

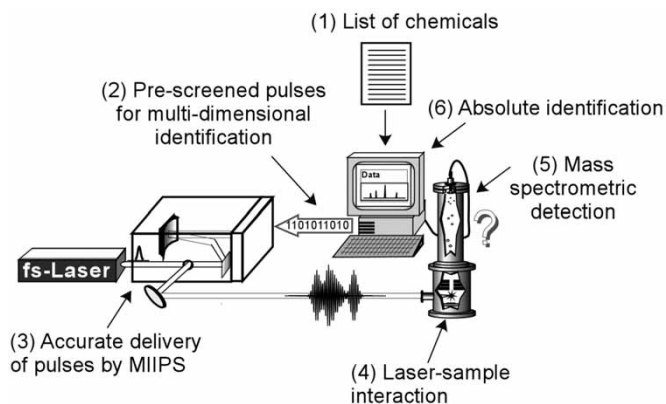


Figure 1. Experimental scheme of point detection. The process starts with the introduction of the chemical into the mass spectrometer. Binary phase functions which have been earlier evaluated as most favourable for inducing relatively large changes in mass spectral fingerprints are then introduced into the pulse shaper where the phase of transform-limited pulses is modulated. The modified laser pulses are then delivered directly to the sample, which then undergoes ionization and fragmentation. The ionized molecule and its fragment ions are subsequently detected by time-of-flight mass spectrometry. A number of binary phase functions could then be used to explicitly identify the chemical.

BPX, where X corresponds to the decimal value of the binary number; i.e. the phase function 0000000000 corresponds to BP0 and 0101101101 corresponds to BP365, where 1 is replaced by π retardation at the corresponding position in the spectrum.

3. Results and discussion

3.1 Phase delivery and performance

Femtosecond laser pulses are very susceptible to spectral phase distortions that are either intrinsic to the laser system or are introduced by dispersive optics in an experimental setup. The elimination of these distortions is especially critical in cases where reproducibility is an important criterion for femtosecond laser applicability. The MIIPS method [3, 9, 10] simultaneously characterizes pulses, corrects spectral phase distortions and delivers accurate and reproducible phase information to a sample. The ability of this method to deliver accurate binary phase functions is illustrated in figure 2, where the excellent agreement between the experimentally recorded and the calculated frequency-doubled spectrum for a binary phase function is shown (in figure 2(c)). The phase function delivered to the sample is illustrated in figure 2(a). When this phase function is applied to the sample without MIIPS correction, significant deviations in the delivered pulses are observed, as shown in figure 2(b). Obviously, phase distortions cause significant changes in the nonlinear optical properties of the pulse and must be eliminated by accurate compensation.

The capability to compensate phase distortions, and consequently eliminate their deleterious effects on nonlinear optical processes is an important parameter for the success of laser-based chemical recognition experiments.

3.2 Experimental search for optimum pulses

A fundamental prerequisite for chemical recognition is finding the femtosecond pulse shapes that provide mass spectral fingerprints for the systematic identification of chemical agents. A typical pulse shaper with 100 pixels (N), can introduce 1000 different phase (N_ϕ), and 1000 amplitude values (N_A) resulting in $(N_\phi \times N_A)^N = 10^{600}$ different pulse shapes to be evaluated. A search space of this size cannot be experimentally sampled because at most 10^7 pulses can be evaluated per day. The most popular approach towards extracting valuable results from the large search space was proposed by Judson and Rabitz [11]. The search, guided by genetic algorithms, has proven to be very successful, especially in cases involving control of chemical reactions [8, 12–14].

The number of variables may be reduced to an experimentally convenient size, while avoiding the loss of all optimal solutions from the search space. The use of

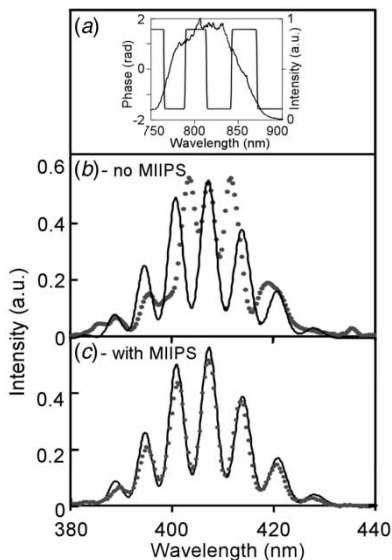


Figure 2. MIIPS performance: experimental data vs. theoretical simulation. (a) Binary phase mask applied to the fundamental laser pulse. (b) Effect of uncompensated pulses. The solid line shows the theoretical frequency-doubled spectrum predicted for the application of the binary phase; the dotted lines correspond to the experimentally measured frequency-doubled spectrum. The disparity between theoretical and experimental measurements is a consequence of erroneous phase delivery. (c) Effect of compensated pulses. The solid and dotted lines represent the theoretical and experimental frequency-doubled spectra, respectively. Note the good correlation between experimental and theoretical measurements when compensated pulses are used.

binary phase shaping [4], in which amplitude shaping is disregarded and only two values (0 or π) of spectral phase are used, allows us to reduce the search space problem to that involving constructive and destructive interference between frequencies [1, 2]. The search space becomes not only considerably smaller but also more readily analysable and amenable to search space mapping [15]. The distribution of the binary phase functions may be mapped to show the phase functions that are optimal for a particular desired interaction, in this case, photoionization and fragmentation of a chemical compound.

Figure 3 shows a search space map [5] which explores a subset of 10-bit binary phase functions and the effects of two of these phase functions on the mass spectral fingerprint of pyridine. A mass spectrum consists of peaks of fragment ions plotted

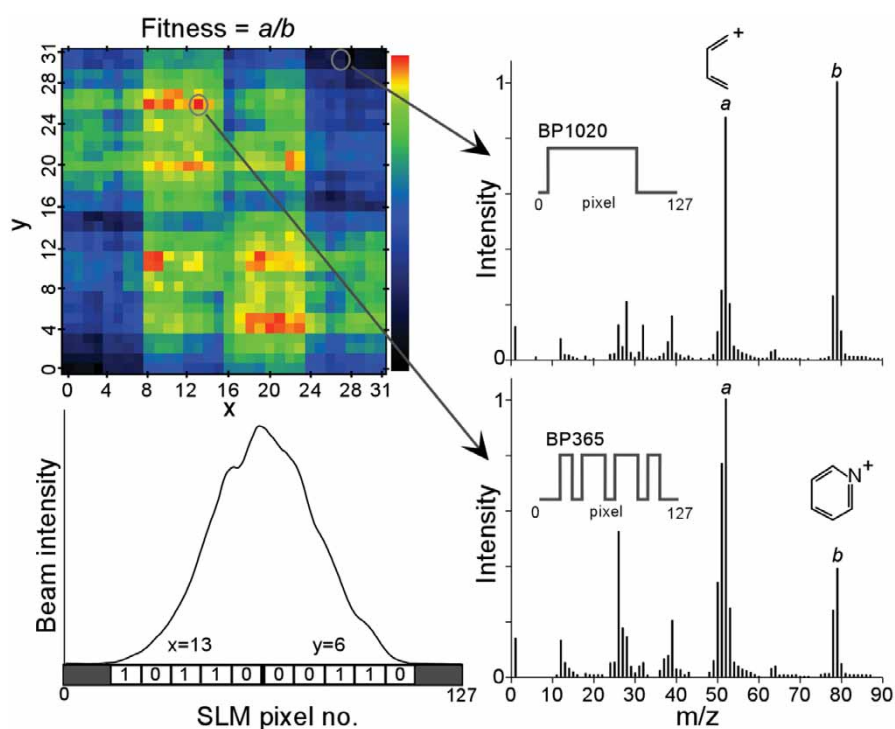


Figure 3. Experimental search space map for the control of pyridine ionization versus loss of hydrogen cyanide, HCN. The map (top left) shows the regions where the fitness (a/b ratio) is highest (red) or lowest (black). The experimental mass spectra obtained with the binary phases BP1020 and BP365 are shown on the right. Notice the large difference in the relative height of peak a ($C_4H_4^+$) resulting from HCN loss, and peak b (pyridine molecular ion). The arrows indicate the position in the map where the highest (red) and lowest (black) ratios were recorded. The bottom left figure shows an example of how a 10-bit binary-phase number is distributed across the spectrum of the laser pulse. The x value for half of the 10-bit phase function and the y value for the other half can be mapped out in the corresponding x and y axes of the search space map. (The colour version of this figure is included in the online version of the journal)

as a function of intensity or yield and mass. Assuming all ions are singly charged and protonated, the mass scale is usually depicted as the mass to charge ratio (m/z). The binary phases shown in figure 3 (BP365 and BP1020) affect the relative intensities of the fragment ion at m/z 52 and the molecular ion at m/z 79 in different ways. The phase functions which generated the highest ratios between these ions are observed in the search space map where the pixels are red. The phase functions which, on the other hand, generated the smallest ratios between the same ions are depicted in black. The identification procedure in this case is two-dimensional, with two different binary phase functions generating two mass spectral fingerprints. When more (n) phase functions are considered in the analysis, the procedure becomes n -dimensional. By looking at the effects of several phase functions on the mass spectrum of a compound, the problem of false positives/negatives, including the need for confirmatory analysis with a different analytical technique can be circumvented.

3.3 Qualitative and quantitative chemical identification

Our results demonstrate accurate identification of a number of molecules in gas-phase mixtures, including chemical agent analogues [6] and pairs of isomeric compounds [7]. Instant visual comparison of mass spectral fingerprints can be achieved through spider plots. At a glance, the phase which provided the greatest change in intensity for a given mass of fragment ion can be detected. The different fragmentation patterns observed for a molecule result from the different laser fields interacting with it. The differences in intensities of the peaks at several mass (m/z) positions highlight the effects of binary phase shaping. Each mass spectrum constitutes a fingerprint that can be used to identify a particular molecule. Figure 4 shows a spider plot representation of the mass spectra obtained for dimethyl phosphite, a nerve agent analogue, subjected to three different phase functions. The ion intensity measurements for each binary phase (BP64 and BP211) were normalized to the measurements obtained using transform-limited pulses (BP0). The deviation of measurements from the octagonal plot of BP0 is indicative of the changes in fragmentation induced by shaped pulses. In addition, the differences observed between the binary phases demonstrate the multidimensional qualitative capability of pulse shaping.

Figure 5(a) shows how various binary phase functions can be used to differentiate between isomeric samples of cresol, nitrotoluene, 3-heptene, xylene and 4-methyl-2-pentene. The ratios between peak intensities of fragment ions at two m/z positions (A^+ and B^+) for each of the isomers change significantly and allow us to predict which isomeric form of a sample is being tested. These intensity ratios (A^+/B^+) were obtained from major fragment ion peaks to ensure statistically acceptable standard deviation values. Much greater ratios (in the hundreds) were observed when minor peaks were considered, but their greater susceptibility to noise diminishes their usefulness for quantitative work. This method is currently being developed further to provide absolute identification of one or more chemical agents in a list of chemical warfare agents.

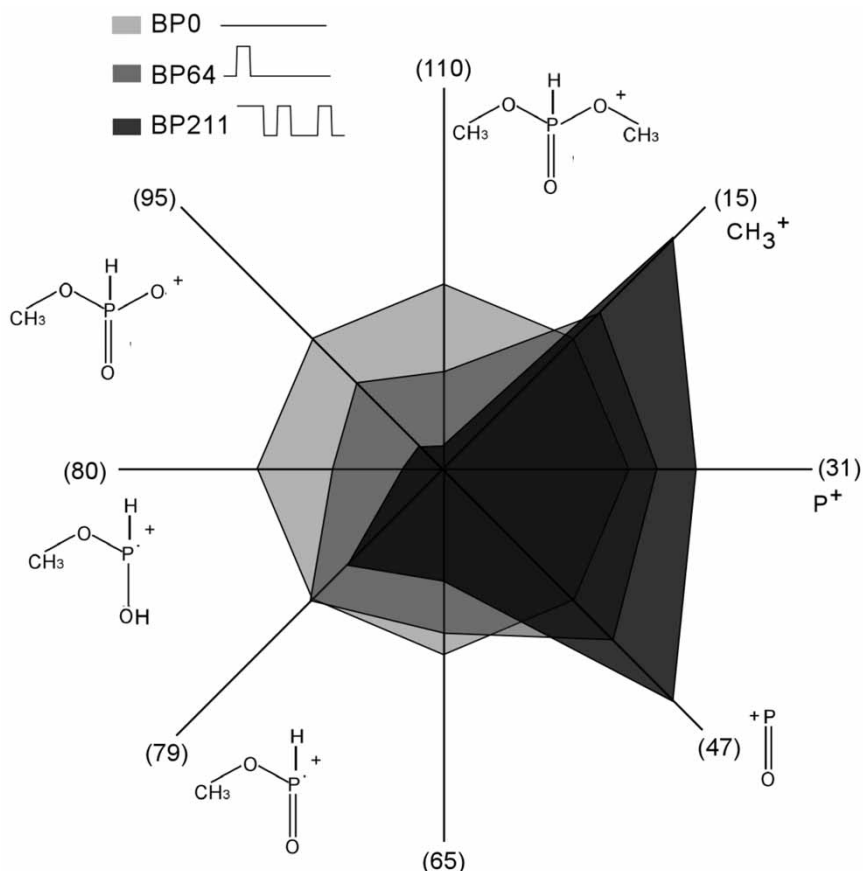


Figure 4. Multidimensional mass spectra of dimethyl phosphite represented as spider plots normalized to transform-limited pulses (BP0, central octagon). Each spoke on the spider plot corresponds to a particular fragment ion, and distance from the centre represents the intensity its intensity in the mass spectrum. Differences in the relative intensity of lines in spectra are evident for two binary phases (BP64 and BP211). Different laser fields yield differences in fragmentation patterns. Note for instance the effect of BP211, where the intensities of fragment ions at m/z 15, 31 and 47 are increased substantially, while the other major fragment ions at m/z 65, 79, 80, 95, including the molecular ion at m/z 110, are considerably decreased compared to transform-limited pulses.

The success of our approach stems from its multidimensional aspect, whereby each shaped pulse in a database performs as an independent dimension of analysis. Experimentally, we have compiled databases for a number of chemical agent analogues. The results from our method also allowed us to distinguish between isomers [7], something that cannot be done using conventional gas chromatography-MS. This multidimensional analytical tool can be used to identify contaminants at low levels in mixtures with greatly enhanced accuracy, an important step in the analysis of a chemically complex environment, and eventually realizing the ideal no-false-positive level [6, 7].

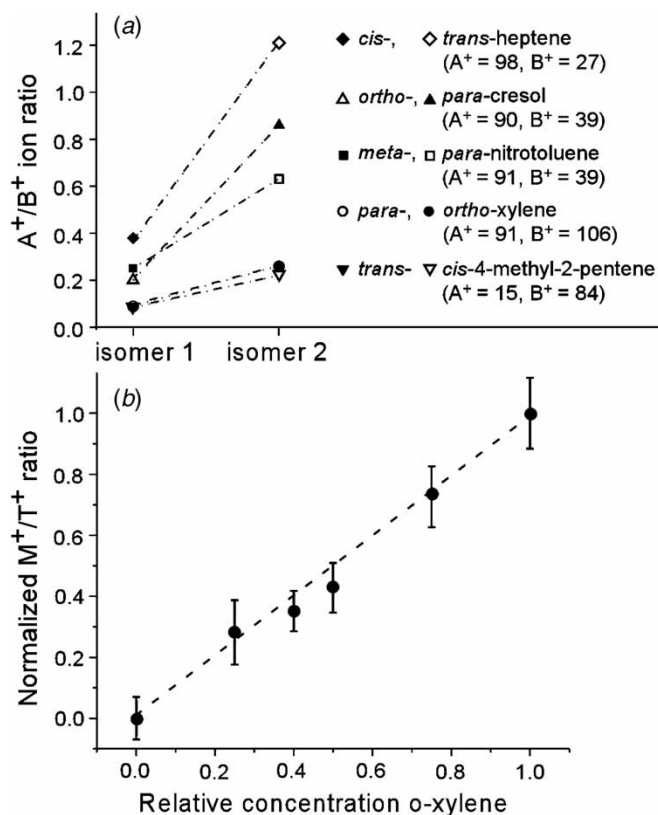


Figure 5. (a) Ion peak ratios obtained for several isomeric pairs using binary shaped pulses: *cis*- and *trans*-3-heptene, *ortho*- and *para*-cresol, *meta*- and *para*-nitrotoluene, *para*- and *ortho*-xylene, and *trans*- and *cis*-4-methyl-2-pentene. The m/z values of the fragments chosen (A^+ and B^+) for each isomeric pair are indicated. The horizontal axis represents the type of isomer used. (b) Quantitative measurement of the concentration of isomeric mixtures using mass spectrometry with shaped pulses. Each data point represents an average of 100 measurements obtained for each of six different mixtures of *ortho*- and *para*-xylene. The horizontal axis corresponds to the known concentration of each of the mixtures. The vertical axis corresponds to the normalized molecular ion, M^+ to tropylium ion, T^+ ratio, which increases linearly with the relative concentration of *o*-xylene. This linear relationship provides a quantitative method to determine the concentration of each of the isomers (*o*- and *p*-xylene) in a mixture. The average values of two sets of data obtained in two different days are shown to illustrate the robustness of this method.

An important component of our method lies in its capability for quantitative analysis. This potential to not only identify but also quantify mixtures is demonstrated in figure 5(b), where the relative concentrations of *ortho*- and *para*-xylene in various mixtures of these isomeric compounds are determined [7]. The linear relationship observed between the relative concentration of the isomer (*ortho*-xylene) and the ratio between the molecular ion (M^+ at m/z 106) and fragment ion at m/z 91 (T^+ , tropylium ion) provides a scheme to predict the

concentration of each of the isomers in a mixture. The reproducibility of the data is convincing enough to increase the analytical merit of our measurements.

4. Conclusions

With accurate delivery of binary phase shaped femtosecond pulses, it is now possible to achieve subsecond, accurate, and quantitative chemical identification while maintaining the extremely high sensitivity of MS. This approach provides a new multidimensionality in MS that is highly sensitive to molecular structure. The unique mass spectral responses of sample molecules to different shaped pulses can be used for their identification by a two-dimensional or N -dimensional approach.

The practical application of our approach is feasible given that a number of one-box, 'no-expert-required' femtosecond lasers are already available that could be used for this purpose. At the fundamental level, our research demonstrates robust laser-based molecular recognition that is made practical by binary phase shaping. These results warrant further development of the method for commercial application. The results should also inspire theoretical studies as to the effect of binary phase shaped pulses on controlling chemical reactions.

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