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Selective nonlinear optical excitation with pulses shaped by pseudorandom Galois fields

Vadim V. Lozovoy, Bingwei Xu, Janelle C. Shane, and Marcos Dantus
Department of Chemistry and Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824, USA
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We demonstrate high-resolution high-contrast nonlinear optical spectroscopy based on phase-modulated ultrashort pulses. The problem of causing selective nonlinear optical excitation at one frequency while minimizing background is framed in terms of low autocorrelation binary sequences. We investigate phase functions with up to 608-bit resolution for their ability to induce two-photon excitation or stimulated Raman scattering, and find the highest theoretical and experimental signal-to-noise ratios yet reported. We confirm our findings by measuring experimental two-photon excitation spectra.

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Controlling laser-matter interactions, which are central to imaging, molecular recognition, nonlinear optics, and material processing, is an active area of research that has lately migrated to the use of ultrashort pulses because of their great efficiency at inducing nonlinear optical (NLO) processes. Controlling NLO excitation requires the design of laser pulses capable of inducing constructive interference between paths that lead to excitation at the desired frequency, while inducing destructive interference between all other paths. Although it is possible to calculate NLO observables such as the *n*th-harmonic spectrum for a given laser field and material, the inverse problem, where one obtains the optimal field explicitly given a desired nontrivial target and an operator expressing the nonlinear interaction between light and matter, has remained in the realm of optimal control theory [1]. A theoretical and experimentally viable solution for selective nonresonant NLO excitation would have broad applications, for example in single-beam selective two-photon microscopy and in high-resolution coherent anti-Stokes Raman scattering (CARS) microscopy. The lack of a mathematical expression that links the desired selectivity to the required properties of the field has motivated the use of empirical methods, such as computer-based search algorithms, for exploring the nearly infinite possible combinations of phase and amplitude functions that define a shaped laser pulse [2]. Here we present theoretical and experimental results in selective NLO excitation that represent the highest resolution and the best contrast ratio yet reported, by orders of magnitude. These results derive from a physical model for NLO, as well as from the unusual combination of nonlinear optics and number theory, as explained below.

Our approach expands on the work of a number of pioneers in the fields of physics and optics. We highlight the work of Weiner, who used periodically repeated binary m-sequences and Dammann gratings to selectively excite coherent phonons in crystals [3,4]. The goal was to generate a pulse train in the time domain to enhance impulsive stimulated Raman scattering (SRS) excitation. Weiner also used shifted m-sequences for a proposed code-division multiple-access network, and m-sequences and Hadamard codes to control second-harmonic generation (SHG) in two-photon diodes and in periodically poled thin or thick crystals [5,6]. The goal was to maximize or minimize SHG at the central frequency. Silberberg used sinusoidal phase modulation and step modulation for two-photon excitation (2PE) of atoms [7,8]. He also used sinusoids, step functions, and phase gates [9,10] to narrow CARS spectra and to suppress nonresonance contributions, taking advantage of the symmetry of phase modulation and of the interference between resonance and nonresonance nonlinear effects [11,12]. Weiner and Silberberg's research focused on maximizing the signal at one frequency without requiring the suppression of the signal at all other frequencies. Optimizing the signal at one frequency while minimizing it at other frequencies is a much more challenging problem, and is what we solve here.

Different approaches have been introduced to achieve selective SRS. One approach involves a pair of chirped pulses [13,14]. In this case, interference between frequencies in the two pulses causes amplitude modulation. Another group of experiments [15–17] and related theory [18] uses a very intense field shaped by a learning algorithm with spectral amplitude and phase modulation. The strong pulse is said to be in the "quasi-impulsive" regime. Our treatment is based on the perturbative regime with broadband laser pulses.

Our interest is in synthesizing the optimal electric field $E^{(2)}$ to cause 2PE and $E^{(0)}$ to cause SRS. These fields are not molecule-specific; nonlinear signals are proportional to the absolute value of the square of these fields and the corresponding molecular cross sections. We define here the two-photon field spectrum $I^{(2)}=|E^{(2)}|^2$ for 2PE, and the intensity spectrum $I^{(0)}=|E^{(0)}|^2$ for SRS, which can be calculated according to the convolution theorem by self-convolution [Eq. (1)] and by autocorrelation [Eq. (2)] of the fundamental field $E(\omega)$ in the frequency domain,

$$E^{(2)}(\omega)=\int E(t)^2\exp(i\omega t)dx=\int E(x)E(\omega-x)dx, \quad (1)$$

$$E^{(0)}(\omega)=\int |E(t)|^2\exp(i\omega t)dx=\int E(x)E^*(x-\omega)dx. \quad (2)$$

The role of phase symmetry in nonlinear optics resulting from these expressions was explored experimentally by Weiner in 1988 for SRS phenomena [3] and by Silberberg in 1998 for SHG [7]. Comprehensive theoretical analysis of the role of symmetry for binary phase shaping has been summarized by Lozovoy [19], and an empirical intuition-based approach to this problem using prime numbers was experimentally explored and published earlier [20].

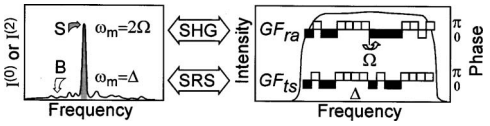

FIG. 1. Selective NLO with phase-modulated femtosecond laser pulses. Left, multiphoton spectrum. The objective is to introduce phase modulation that maximizes the nonlinear signal S only inside a narrow window and minimizes the background B elsewhere. Right, spectrum of the laser pulse in the frequency domain and two different symmetrized Galois fields.

We find that the problem of maximizing the NLO signal at one frequency while minimizing the background elsewhere can be framed in terms of the number theory problem of finding low-autocorrelation binary sequences. To see this link, we first simplify the problem for theoretical analysis by assuming that the spectrum of the fundamental field is unity for all frequencies, and we concentrate on the electric field, leaving molecular cross sections aside. The use of binary phase shaping, in which the spectral phase is limited to values of 0 or π, allows us to represent the electric field (E_i) in the frequency domain as a sequence of values +1 and −1, respectively. This mathematical object forms a Galois field GF(2^N), where N is the number of bits in the sequence. Equations (1) and (2) can be rewritten for Galois fields as Eqs. (3) and (4),

$$E_{i+j}^{(2)} = \sum E_i E_j;\ i = 0, \ldots, N-1, j = 0, \ldots, N-1, \qquad (3)$$

$$E_{i-j}^{(0)} = \sum E_i E_j^*;\ i = 0, \ldots, N-1, j = i, \ldots, N-1, \qquad (4)$$

Equations (3) and (4) summarize how Galois fields can be used to suppress NLO excitation at any desired frequency simply by having an equal number of +1 and −1 contributions in the sum. Binary sequences with minimum autocorrelation will minimize the sum for every frequency; when symmetrized or antisymmetrized, they will produce maximum NLO excitation at their center of symmetry while suppressing excitation elsewhere, exactly as desired in selective NLO excitation. The amplitude of the resulting spectrum is bound at all frequencies by the spectrum of a transform-limited (TL) pulse $E_i=1$ such that $E_{N\pm i}^{(2)}=E_i^{(0)}=N-i$. We can therefore produce selective NLO excitation through the use of minimum-autocorrelation binary sequences, which are freely available thanks to the years of research in the well-established fields of communications engineering and statistical mechanics [21].

Figure 1 describes how to use phase shaping of an ultrashort pulse to achieve selective NLO excitation. First, we choose a pseudorandom binary number from a list of sequences with minimal correlation [22] (for N=8, for example, it is 10110000). Second, we transform the binary number into a GF(2^N) sequence (−+−−++++). Third, we symmetrize (or antisymmetrize) the GF, depending on the nonlinear process, using reflection $GF_{ra}(2^N)$ for 2PE and translation $GF_{ts}(2^N)$ for SRS, producing a phase function that will cause the desired selective NLO excitation.

Using the above method, we have tested solutions of Eqs.

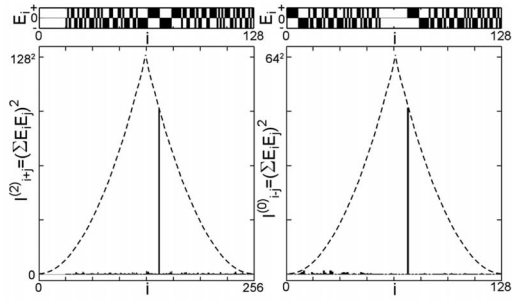

FIG. 2. Symmetrized pseudorandom Galois fields (left) and their self-convolution and autocorrelation (right) for the generation of very narrow NLO excitation with minimum background in SHG or SRS spectra.

(3) and (4) using binary sequences of length up to 608 bits. The results are described in terms of two parameters: signal-to-noise ratio (S/N) and contrast ratio (CR), as shown in Fig. 1. S/N compares the peak signal to the average background, while CR compares the integral of the signal peak divided by the integral over the entire background, a measure that is important when this method is used for scanning 2PE spectroscopy. The optimal 608-pixel solution created using a symmetrized low- autocorrelation 304-bit binary sequence is
++++−+−+++−−+++−+−−−+−−−+−+++−−−
+−−+++−+−−−−+−−+−+−−−+−−+−−−+−−−−−−−−
−++−++−−+−−+−+−+−−−−−+++−−−+++++−−+
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−−++−++++++−+−. The resulting Galois field gives a S/N of 1697:1 or 1400:1, and a CR of 1.4 or 2.3 for 2PE or SRS, respectively. These pseudorandom binary sequences provide at least three or seven times better S/N and CR than the average completely random binary phase function for a given number of pixels for 2PE and SRS, respectively. The improvement is up to 50 standard deviations above the mean. This level of performance would be virtually impossible to achieve using random binary phase functions. This performance would also be extremely difficult to reproduce using a learning algorithm controlled pulse shaper. Although some of the low-autocorrelation binary sequences given in [22] were found using learning algorithms, finding low-autocorrelation binary sequences is a very challenging problem that requires the use of multiprocessor computers. The longest low-autocorrelation binary sequences (with $>10^6$ digits) have been designed using Legendre sequences [23].

When the signal to be maximized is not in the center of the spectrum, we form the GF from the longest possible symmetrized sequence. The leftover GF bits, which do not contribute to the signal, must be set to 0 by amplitude modulation. This decreases the background without changing the maximum NLO response for 2PE, and suppresses the low-frequency half for SRS excitation. Results of calculations according to these rules are presented in Fig. 2. As the number of bits in the GF sequence increases, the amplitude of the signal remains at the TL limit (dashed lines in Fig. 2), pro-

vided symmetrized sequences are used. At the same time, the mean amplitude of the background, as well as the width of the signal peak, decrease linearly with the number of pixels. Multiphoton intrapulse interference [24,25] is responsible for the almost complete background suppression. Thus, without resorting to empirical evaluation, we are able to construct excellent solutions to the problem of selective NLO excitation. In the case of an ideal pulse shaper, our work is finished at this point. The second, experimental part of this paper deals with compensation for the optical imperfections of our pulse shaper.

Experimental measurements were carried out with a Ti:sapphire oscillator capable of producing 10 fs pulses (110 nm full width at half-maximum) centered at 800 nm and 250 mW average power. The laser was precompressed by a folded pulse compressor consisting of a pair of SF10 prisms. The pulse shaper, consisting of a SF10, a BK7 prism, a 200-mm focal length cylindrical mirror, and a dual-mask spatial light modulator (SLM), is based on the general design of Weiner [26] in a reflective geometry. To achieve accurate phase retardations, each pixel of the SLM was calibrated by measuring the polarization-dependent transmission of light. The spectral resolution for the fundamental in this experiment was 1.5 nm/pixel. The multiphoton intrapulse interference phase scan (MIIPS) method [27,28] was used before each experiment to compensate at the target any spectral phase deformation inherent to the laser system or introduced by the optics. With this setup, were able to deliver phase functions with 0.05 radian precision.

We focused the beam on a 10 μm β-BBO type I crystal. The resulting SHG signal was recorded with a spectrometer and provided $I^{(2)}=|E^{(2)}|^2$. We recorded the second-order autocorrelation trace, measured with a balanced Michelson interferometer. According to the correlation theorem, the Fourier transform of the second-order autocorrelation provides $I^{(0)}=|E^{(0)}|^2$.

To demonstrate the analytical solutions to Eqs. (3) and (4) under experimental conditions, we performed experiments with sequences of length $N=48$ bits distributed over the center of the SLM, where the spectral laser power is greater than $\frac{1}{4}$ of the maximum value; frequencies outside this range were blocked. The spectral width of the remaining portion is 70 nm. Initial experiments were performed using symmetrized GF based on sequences with minimal autocorrelation [22]. Very narrow peaks in 2PE and SRS spectra were observed. The intensity of the peaks was about 70% of the transform limited intensity. Simulation shows that the nonlinearity of spatial to frequency transformation in the pulse shaper decreases the maximum of the peak in the NLO spectrum, and that SLM spectral resolution is responsible for the less-than-ideal background suppression.

To optimize S/N, we first calculated correlations for all symmetrized 24-bit Galois sequences with a 4-bit flat region at the beginning. This gave us a total number of $2^{(48/2)-4}$ sequences to evaluate, a number that is very small compared to the number of 48-bit phase functions with arbitrary phase and amplitude modulation. We simulated the best sequences to predict their NLO response, taking into account the spectrum of the fundamental pulse and the two main imperfections of the SLM, nonlinearity of dispersion, and limited spectral resolution. By this method, we optimized selective NLO at a number of different frequencies outside the center of the bandwidth so that we could scan the excitation frequency.

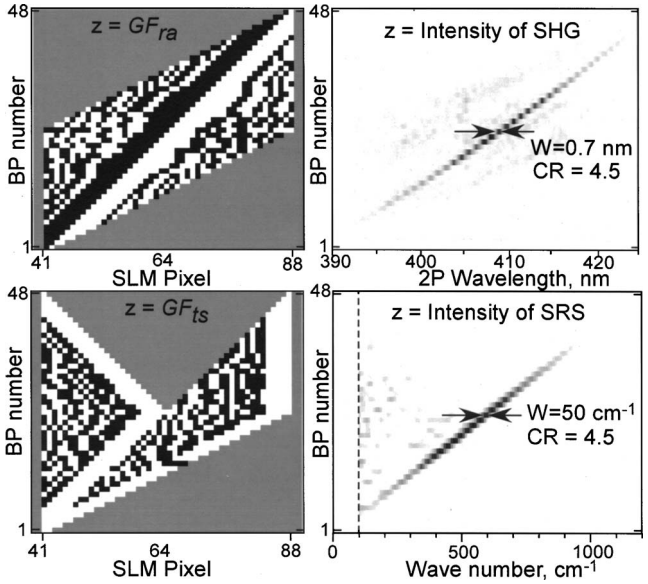

FIG. 3. Experimental NLO excitation. Left (top and bottom), phase masks imprinted on the SLM. Each horizontal row represents different phase shapes, which are shown along the y axis in order of increasing target frequency for selective NLO excitation. Black corresponds to −1, white to +1. Gray areas are regions where the amplitude of the field was set to 0. Right, experimentally measured SHG (top) and SRS (bottom) spectra; darker shading indicates higher intensity.

Our experimental results are presented in Fig. 3, where we scan a narrowband peak with an S/N of 150 and a CR of 4.5, the highest ever reported in selective NLO excitation by a single phase-shaped ultrashort pulse. Compared to a sinusoidal phase modulation, which produces an S/N of 3 and a CR of 0.4, these results show improvement of almost two orders of magnitude. The narrowband peak has a spectral width of 0.7 nm in 2PE and 50 cm^{-1} in SRS spectra, which is close to the spectral width of one SLM pixel, this being an experimental-limiting parameter.

We demonstrate the application of the solutions found for selective two-photon excitation by measuring the 2PE spectrum of several molecules in solution. To obtain the normalized intensity 2PE spectrum, we scanned a series of optimized GF sequences and measured the ratio between two-photon laser-induced fluorescence and the SHG intensity obtained by the same laser pulse when focused on a thin crystal. In Fig. 4, we show the 2PE spectra for Coumarin 460 and Rhodamine 590 in methanol ($10^{-5}M$). The results obtained here by pure phase shaping are in good agreement with independent experimental measurements [29]. We also measured the 2PE spectra of 8-hydroxypyrene- 1,3,6-trisulfonic acid (HPTS) in $10^{-2}M$ H_2O buffer (515 nm emission) at two different pH's. The differences in 2PE spectra for this fluorescent probe under different environmental pH conditions have been used by our group to demonstrate selective excitation in two-photon microscopy and in two-

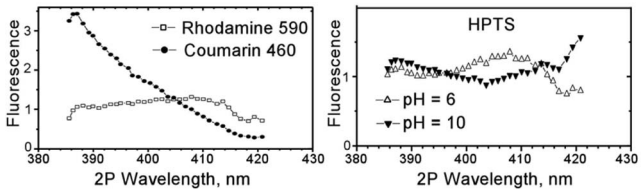

FIG. 4. Normalized 2PE spectra of two fluorescent dyes (left), 2PE spectrum of acid and basic solution of *p*H sensitive probe HTPS (right).

photon imaging through biological tissue using pulse-shaping methods [30–32].

In conclusion, we present a general solution (and a specific 608-bit solution) to selective even-ordered multiphotonic excitation. We discovered that using low-autocorrelation binary phase sequences allows us to achieve selective nonlinear optical excitation while suppressing background. The existing literature on low-autocorrelation binary numbers provides sequences that can be used to construct phase functions that will optimize excitation. In this way, we avoid using empirical evaluation-based searches that scale exponentially with the number of pixels. As a first application, we obtained experimental two-photon excitation spectra. Selective nonlinear excitation will allow coherent anti-Stokes Raman scattering and photon echo spectroscopy with a single laser pulse. Other applications exist in photochemistry and biophotonics, including functional multiphoton microscopy and selective two-photon photodynamic therapy. With the adaptation of number theory principles to physics and chemistry, progress in modern mathematics together with technical progress in controlling the phase of laser light promise the development of new nonempirical approaches to laser control of physicochemical processes. We chose the sequences with best CR from this simulation for experimental evaluation.

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