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Application of parametric time and frequency domain shaping

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Abstract. We present two novel types of parameterizations for optical control experiments, executed by pulse shaping and evolution strategies on the NaK system. The first is a time domain approach with a pulse parameterization with few, intuitive parameters such as temporal subpulse distances, energies, chirps, and phase differences. It will address the reproducibility and complexity issues that occur when employing non-deterministic algorithms in complex search spaces. The second approach, a 'transition finder' algorithm uses a parameterization in the frequency domain to expose the most important transition frequencies within the laser pulse spectrum, which would not be found otherwise.

PACS. 82.53.-k Femtochemistry – 33.80.-b Photon interactions with molecules

1 Introduction

Laser pulse shaping has produced very interesting results in the field of molecular dynamics in the last years [1]. Recently, not only control of chemical reactions [2–5] became feasible but also progress in understanding the solutions obtained by feedback-loop experiments has been made [6,7]. One reason for employing general search algorithms in optimal control experiments [8] is the fact that the exactness of the studied potential energy surfaces is not high enough to calculate reliable electric fields. Taking advantage of the full search space of a femtosecond pulse shaper[1] often leads to highly structured and complex results. Complexity and reproducibility issues are the two main disadvantages of the otherwise rather successful and universal tools of genetic algorithms. To simplify the results and address the inversion problem, a reduction of search space seems to be the most logical way to start. It should, in principal, be able to obtain the minimum number of parameters for control; so far, attempts were made using principal component analysis [9] and correlation-techniques [10].

As any parameterization selects a subset of search space in a more or less defined and imaginable way, also the outcome is strongly determined by the type of restriction. The advantage is that it is possible to choose the 'framework' of an experiment, and let it no longer only being constituted by the physical set-up. The additional control gained together with the feedback loop concept enables one to 'ask' the experiment certain questions. Having already some physical knowledge at the back of one's mind, one can choose a parameter set for an intended purpose, knowing that the results will also be found within this subset.

The most basic reduction is attained by reducing the experimentally most accessible control values. For a spatial light modulator (SLM), combining adjacent pixels or quantizing the pixel phase values has demonstrated to manageable influence the outcome while improving convergence speed and robustness under noise [11]. A nice example is given in reference [12] for non-resonant two-photon interactions, where different solutions of the spectral phase, parameterized by $\Theta(\Omega) = \alpha\cos(\beta\Omega)$, lead to an enhancement/cancellation of the two-photon transition probability (with bright and dark pulses); similarly performed on atomic Na [13]. A time-domain representation of the pulse structure allowed to implement different parameterizations that each represent certain control mechanisms [14] for degenerate four-wave-mixing in K_2. Symmetrical pulse trains in time were used to reduce the complexity of the results from NaK ionization experiments in a step-by-step manner [15]. Fluorescence from laser dye molecules in solution optimized by an acousto-optical modulator was reported from [2], where three parameters of a single pulse were employed.

Here, we apply two novel types of parameterizations in the time and frequency domain on the model-system NaK, which, in the meantime, is well enough understood to try and test new control schemes.

2 Experimental set-up, algorithm

The system investigated for this paper is NaK in the gas phase, at a wavelength of 780 nm. The dimers are prepared

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[1] 256 pixels having each 1000 different voltage values span a search space of 10^{768} points.

in an adiabatic coexpansion of the metal vapors at approx. 600° C into the vacuum through a nozzle and are propelled by argon as a carrier gas [16]. The fs-pulses are delivered by a Spectra Physics Tsunami oscillator, the bandwidth amounts to 6.4±0.1 nm. The pulse intensity around 1 GW/cm^2 (energy of about 10 nJ) allows the experiment to be treated in the weak field regime. A quadrupole mass spectrometer and a secondary electron multiplier detect the cluster ions. The 2×128 pixel SLM (CRI) is situated in the Fourier plane of a zero dispersion compressor and is capable of performing phase and amplitude modulation simultaneously and independently.

The non-elitist algorithm (based on evolution strategies) starts with random values, the population consists of 10 parents that produce 30 offspring each generation. The operators that act on all the newly produced individuals are uniform cross-over and self-adapted mutation, sequentially.

3 Parameterization in the time domain

Time-domain mappings are sometimes considered as 'direct' connection to the electromagnetic field of a laser pulse. Experimentally, the shaping process is conducted by altering the spectral field of the pulse, and for the foreseeable future, direct control of light fields in the time-domain seems difficult to achieve (only recently, a direct measurement [17] was reported). We construct the complex electrical field of a pulse train by [13]

$$\tilde{E}_{out}(t) = e^{i\omega_0 t} \sum_n \varepsilon_n(t - t_n) e^{i\varphi_n(t)} = e^{i\omega_0 t} \sum_n \tilde{\varepsilon}_n(t - t_n) \tag{1}$$

(valid for pulses having the same central frequency ω_0; ε_n and $\tilde{\varepsilon}_n$ are the field envelope and the complex field amplitude of the subpulses, respectively, the t_n are the pulse distances in time). The resulting temporal field is then Fourier transformed to obtain $\tilde{E}_{out}(\omega)$. With a linear filter such as the SLM, the complex filter function to result a desired output pulse is $\tilde{H}(\omega) = \tilde{E}_{out}(\omega)/\tilde{E}_{in}(\omega)$. The possible waveforms are limited by physical set-up issues [18] like pixel quantization, laser bandwidth, gap-to-stripe ratio, and phase resolution, leading to a maximum complexity of the pulse, to pulse replica, a limited temporal shaping window and to other side-effects [19].

The experiments are performed using only phase modulation (to keep the pulse energy constant), such that $|\tilde{H}(\omega)| = 1$. Due to this constraint, no exact transfer function can be determined for those transformations which require a change of spectral amplitudes. A reliable algorithm that approximates a desired temporal pulseform using a fast iterative routine [20] that implements the Gerchberg-Saxon-Algorithm [21], is included in the *Lab2* package [22].

For the experiments, we break down the full search space to an 11 or 23 parameter space; the pulses described herein consist of three/six subpulses (inspired by previous results from unrestricted (free) optimizations [16]).

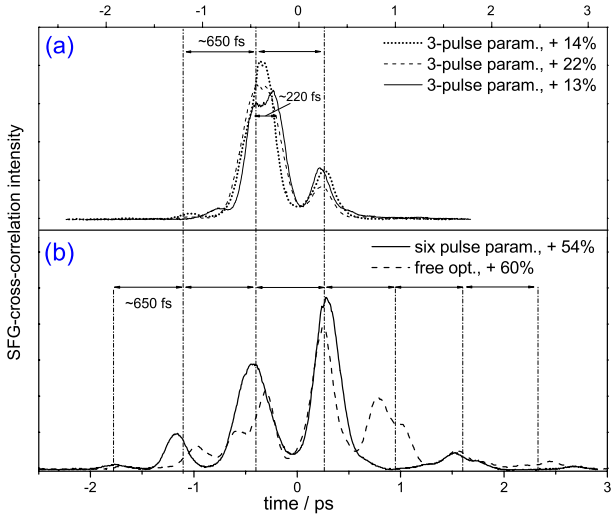

Fig. 1. SFG-CC traces of the optimized pulse shapes. (a) Three subpulses have been permitted to improve the ionization efficiency. (b) Six pulse parametric optimization compared to the result from free phase-only optimization on NaK. Most pulse distances amount to 1.5 T_{osc} of a wavepacket in the A(2)$^1\Sigma^+$ state.

The subpulse distances were limited to a range from 180–2000 fs, their energy ratios were allowed to reach a maximum contrast of 1:10 at the center of the temporal shaping window. The subpulse linear chirp was restricted to a range from −20000 to 20000 fs^2, the peak zero order phase was given the full potentiality $0-2\pi$. This phase represents the relative position of the rapid field oscillations with respect to the envelope. The phase difference of locked subpulses plays a crucial role [23] as it manifests in possible constructive or destructive wavepacket interference, and therefore has to be included in such parameterizations as a necessary degree of freedom. Due to the improved convergence speed because of the significant parameter reduction, one experiment takes no longer than a few minutes.

The three pulse experiment is shown in Figure 1a. We plot the sum-frequency-generation cross-correlations of three coinciding waveforms; featuring pulse distances of 650 fs, which corresponds to 1.5 T_{osc} of the excited wavepacket in the A(2)$^1\Sigma^+$ state (440 fs). For all three shown pulses there is, however, a double-pulse structure with a distance of about 220 fs at the limit of the temporal resolution embedded within the main peak which can be made out from small 'bumps' on main pulse, visible in the XFROG [24] traces and the algorithm parameters. According to our previous results [16] a scheme of the optimized ionization processes can be proposed.

The first small subpulse (an unintended, so-called pulse replica) transfers some population from the solely populated X(1)$^1\Sigma^+$ ground state to the first excited A(2)$^1\Sigma^+$ state. After about 1.5 oscillation periods, the excited wavepacket is located at the outer turning point and the first of the two main subpulses arrives, which transfers from there to the NaK$^+$ ionic state via a resonant

two-photonic transition. Furthermore, it also transfers again from the ground to the first excited state. The second main pulse that arrives about 220 fs afterwards ionizes the previously created population at the outer turning point. The last subpulse arrives after about 1.5 oscillation periods, and again ionizes the remaining population created by the first of the main double pulses.

In Figure 1b we ask a different question, namely what the optimized pulse would look like when the algorithm was granted the liberty to arrange six pulses, with constraints otherwise the same as for Figure 1a. The six-pulse parametric optimization has a higher ionization efficiency to offer, and the subpulse distances, again, amount to approx. 650 fs. Recent theoretical calculations [25] showed that at a wavelength of 770 nm (using potential energy surfaces from [26]) 'later' subpulses have a significant impact on the population of the ionic states due to wavepacket propagation in the intermediate $B(3)^1\Pi$ state. We conclude that a repeated, stepwise excitation is likely to yield the better results.

The unrestricted optimization at 780 nm produces a comparable waveform except for one more peak (at around 0.8 ps) and a slightly higher ionization yield. It is likely that the remaining differences between the free and parametric results originate from the search-space restriction and/or aberrations at the edge of the temporal shaping window (Nyquist-limit). However, this convergence to results from a free, unrestricted optimization shows the potential of the introduced method to gradually gain knowledge about molecular systems.

4 Transition finder (frequency and time domain)

The amplitude parameterization presented portrays a different approach as it tries to point out the transition frequencies that are most important within a specific wavelength range. When performing experiments with phase and amplitude modulation in order to maximize the ion yield of a single molecule, the optimized pulse shaper patterns often exhibit the full transmission over the illuminated zone and random values outsides. As long as there exists a positive correlation between the pulse peak intensity and total ion yield [10] the algorithm senses no improvement in 'reducing' certain amplitudes. Transition frequencies can therefore be found by 'pulse cleaning' [27, 28] where the fitness function is manipulated in order to diminish less important frequencies — which can be regarded as a complimentary approach to the one presented here.

Our method tries to find the optimal pulseform for ionization under the restriction that only a few single pixels are permitted to be transparent, the others are set to maximum attenuation; we used eleven narrow Gaussian amplitude distributions to be identified. The parameters were the distance of the pixels to the central frequency (they were allowed to overlap), and their respective transmissions. Apart from this simplification, these experiments correspond to an amplitude-only measurement.

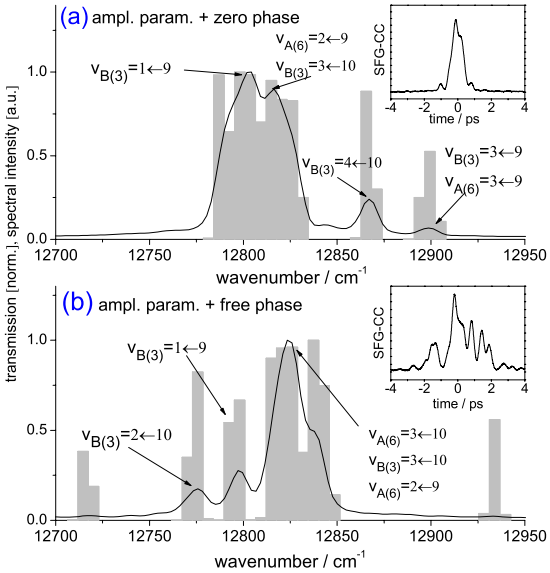

Fig. 2. Peak finder algorithm. It points out the most significant transitions within the laser bandwidth. (a) Depicts the findings for an amplitude-only search, in (b), the phase is added to the search. The grey bars represent the pixel transmission and the solid line the spectral intensity. The insets show the temporal pulse shapes.

We applied the method on NaK in order to identify the otherwise obstructed electronic pathways. Figure 2 displays the findings. Graph (a) shows the transitions that were identified by the algorithm. Both $A(6)^1\Sigma^+ \leftarrow A(2)^1\Sigma^+$ and $B(3)^1\Pi \leftarrow A(2)^1\Sigma^+$ transitions occur and are possibly both utilized to effectively ionize the system at the inner turning point (direct three-photonic ionization).

For another experiment, we additionally allowed the phase to evolve freely in order to allow a temporal expansion of the pulseform (Fig. 2b). Except for the center peaks around 12825 cm^{-1}, we found very different transitions and can explain this by the different Franck-Condon-factor at the now available outer turning point [29], which emphasizes the significance of the temporal evolution set off by the fs-pulse.

5 Conclusion/outlook

The introduced methods are intended to serve as additional tools to investigate molecular dynamics on the femtosecond timescale. They feature an improved convergence speed with physically intuitive restrictions/parameters.

With the transition finder we demonstrated that we could expose electronic transitions to particular vibrational states which are usually 'hidden' in a closed loop experiment's fs-pulse spectrum and to obtain helpful information about the chosen ionization path.

Compared to other parameterizations like sinusoidal or polynomial mappings of the spectral phases, the introduced temporal parameterization not only offers more shaping possibilities but also much more clarity about the

restrictions to search space one is imposing. We could show that a more complicated, six-subpulse waveform approaches the results from free optimization which demonstrates the method's utilizability for approaching more complex systems in a step-by-step manner.

In the future, an initial guess pulse from theory could be integrated, parametrically varied, and extended. Furthermore, a restricted optimization could be employed to forbid certain ionization paths/potential energy surfaces and to make the algorithm find the best solution under these special circumstances. Transitions via particular vibrational states could be favored or excluded, and certain dissociation/reaction paths could be specifically addressed.

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