On the paradigm of coherent control: the phase-dependent light–matter interaction in the shaping window

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**Abstract.** Coherent control is unquestioningly a powerful method to investigate the interaction of femtosecond light pulses with ultrafast molecular processes. In order to exploit to a great extent the capabilities of coherent control, a judicious analysis of experimental control results is required, which is especially true for the manipulation of matter waves with phase-locked femtosecond pulses. Due to its importance for the optical control of chemical reactions, we discuss the tailoring of wavepackets and the interpretation of such coherent control results in the region where the pump and probe pulses temporally overlap. In this region, called the shaping window, the observed dynamics are phase dependent and may misleadingly resemble oscillatory molecular dynamics. In a transient absorption experiment, part of these oscillations is successfully identified as intra-multipulse interferences and the phenomenon is qualitatively and quantitatively explained by the spectral appearance of the unshaped laser pulse. Furthermore a strategy is presented based on phase-cycling for easy differentiation between interference effects and true wavepacket dynamics. These new findings have important consequences for the interpretation of adaptive coherent control results.

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1. Introduction

The ambition to optically control chemical reactions has been instigating the use of coherent control to manipulate matter wavepackets in the gas as well as in the liquid phase [1]–[9]. Together with the first control experiments using chirped pulses [10], double pulses [11] and in particular multipulse sequences have been shown to promote vibrational or rotational wavepackets. In this context, the periodicity of wavepacket phenomena found in bound electronic states provides an intuitive scheme for their manipulation. The temporal spacing between the sub-pulses of a pulse sequence causes the effect of filtering out vibrations whose period does not coincide with sub-pulse spacing, achieving this way selectivity of molecular degrees of freedom [12]. This general control mechanism of light–matter interaction was used in coherent anti-Stokes Raman scattering and later further exploited in microscopy [13, 14]. Depending on whether the excitation is electronically resonant or not, pulse trains can also enhance molecular vibrational coherence as well as the population transfer to excited electronic states [15]–[18].

In this framework, extensive sequences of pulses are also found, very often in adaptive coherent control experiments of complex molecular systems, e.g. the energy flow in the light harvesting complex [19], artificial antenna systems [20], isomerization of retinal [21] and cyanine dyes [22], as well as breathing modes of fullerenes [23]. In the search for a mechanistic explanation, it is tempting to relate the optimal pulse shape and its sub-pulse spacing to the filtering and/or enhancement of a particular vibrational mode(s). However, in very few cases it was possible to demonstrate by parameterization [24] that indeed a wavepacket filtering effect was taking place [17, 19]. Several alternative techniques have been developed and applied particularly to closed loop coherent control [25], but its applicability was limited to constrained or simple chemical systems [26, 27]. More recently it was also discussed that the transient signal, recorded for time delays shorter than the characteristic timescales of the quantum mechanical system, holds the effect of the pump pulse’s spectral phase and, therefore, is expected to help to reveal the control mechanism [28, 29]. In this paper, we will show that the unravelling of the control mechanism in the region where the tailored pump and probe pulses overlap, called here shaping window (SW), requires a detailed analysis. We discuss the possibility of experimental observation of the control mechanism in a transient absorption (TA) experiment using a simple prototype system (Nile Blue) in solution. The observed phenomena will be explained in the framework of a modulation of the multipulse envelope and its effect on the TA coherent signal, particularly with respect to the different spectral excitation shapes. Finally, a possible phase-cycling method for minimizing this effect is successfully implemented.
2. Experimental details

Our transient absorption setup was already described in a previous publication [18]. Briefly, the pump and the probe pulse were generated in two separated home-made non-collinear-optical parametric amplifiers (nc-OPA), generating ultrashort pulses with durations below 15 fs. Time resolution was measured in situ by cross-correlation using a two-photon sensitive photodiode and found to be around 20 fs [30]. After resonant excitation, the transient absorption signal was collected at the maximum of the bleach signal of the $S_0\rightarrow S_1$ transition ($620 \pm 5$ nm) using a single low-noise amplified photodiode.

The pump and probe beams were focused with the same concave mirror ($f = 20$ cm), giving a photon flux in the range of $4 \times 10^{14}$ photons cm$^{-2}$ per pulse. In this energy regime, the transient absorption signal shows linear intensity dependence as checked prior to the control experiment.

The pump pulse $\tilde{E}_{\text{in}}(\omega)$ was phase modulated with a liquid crystal spatial light modulator (CRI SLM 256 pixels) using a sinusoidal phase function $\phi(\omega)$ to obtain a multipulse sequence with variable phase parameters:

$$\tilde{E}_{\text{out}}(\omega) = \tilde{E}_{\text{in}}(\omega) \cdot e^{i\phi(\omega)},$$

with $\phi(\omega) = a \cdot \sin[b \cdot \omega + c]$. The factor $a$ defines the relative amplitude between the sub-pulses. According to [31], a value of 1.23 guarantees the best multipulse modulation (i.e. contrast between maxima and minima) for a given spacing and initial pulse duration. The modulation period $b$ corresponds to the temporal spacing between the sub-pulses. This spacing was explored in a previous work to show the relation between tailored near-resonant excitation and enhancement of electronic population and vibrational coherence [16, 18]. In this work, it was set to 56 fs, which corresponds to the vibrational period of the ring breathing mode of Nile Blue ($\sim 600$ cm$^{-1}$). The phase parameter $c$ affects the relative phase between the sub-pulses and is discussed below to access the molecular dynamics.

Shaping artefacts due to space–time coupling [32]–[35] were carefully checked in all measurements using a beam analyser to image the pump beam profile in the focus position. Therefore, space–time coupling effects can be excluded for the phase function used in this work. Furthermore, optical artefacts like coherence spikes were tested in pure solvent and their amplitude was smaller than 1 mOD.

Nile Blue (LC6400) was purchased from Lambda Physik and dissolved in methanol (Fluka, HPLC) without any further purification. Sample’s optical density was 0.5 OD. In order to minimize light scattering and therefore to improve signal-to-noise ratio, the solution was filtered with 0.2 $\mu$m filter (PTFE). The sample cell was a 0.5 mm thick quartz cell (Hellma).

3. Results and discussion

Figure 1(b) shows transient absorption signals for Nile Blue when excited with a tailored pump as shown in figure 1(a). The signal exhibits a long-lived $S_0\rightarrow S_1$ bleach signal, superimposed by strong oscillations with a period of 56 fs ($\sim 600$ cm$^{-1}$). This vibrational coherence dephases within a few picosecond timescale depending on the solvent [18], [36]–[38]. It is tempting to associate all observed oscillations of the signal to the breathing mode of Nile Blue. However, when the parameter $c$ is varied from 0 to $\pi$, the oscillations for long probe delays (>0.15 ps) remain the same (figure 1(b)). Just for the temporal range when the shaped excitation pulse is
Figure 1. The influence of shaped multipulse on molecular dynamics. (a) Cross-correlation between shaped pump and probe pulse. (b) Transient absorption signal of Nile Blue’s ground state bleach measured with sinusoidal phase for several values of the phase parameter $c$. Black and red curves indicate the lower and upper values of a $c$-scan between $c = 2.35$ and $5.5$ rad, respectively. (c) The residual TA signal after the subtraction of the slow population dynamics is shown for two multipulse sequences with the parameter $c$ differing by $\pi$.

present, indicated as SW in figure 1, we observe a modification of the phase and amplitude of the oscillations. This $c$-dependence becomes even more evident if the slow population dynamics is subtracted from the experimental transient using a global fitting with a single rise and decay constants for all transients. This can be observed in figure 1(c), where the residuals of this subtraction for two multipulse sequences (with parameter $c$ differing by $\pi$) show a very complex modulation within the SW. The absence of any effect on the transient absorption signal outside the SW indicates that the oscillations inside the SW have additional contributions other than just wavepacket motion. Within this region, coherent as well as sequential transient signals in the form of molecular vibrations initiated by each individual sub-pulse contribute to the signal [39, 40]. Additionally, we can identify significant contribution of the phase-sensitive temporal interference between the sub-pulses. We called this effect multipulse envelope modulation (MEM), which will be discussed in the following. The MEM is related to other interference
Figure 2. Dependence of the sub-pulse interferences on the pulse spectrum. Multipulse sequences with 56 fs period were simulated from four different pump spectra: experimental (a), squared (d), Gaussian (g) and a mixture of 1/3 squared + 2/3 Gaussian-shaped spectra (j). The respective temporal intensity patterns are shown below each spectrum for two different values of the parameter $c$: second row with $c = 0$ (b, e, h and k) and third row with $c = \pi/2$ (c, f, i and l). The multipulse sequences were normalized by the maximum value of each sequence with $c = 0$.

effects as the generation of coherent transients with shaped pulses [41]–[43] and intrapulse interference [44].

In order to extract the influence of MEM on the transients in the SW, we analysed the phase dependence for different spectral shapes of the pump pulse. In this context, the MEM can be well described if the experimental excitation spectrum is parameterized in terms of a Gaussian- and a squared-shaped spectrum. Figure 2 compares the MEM at two different values of the parameter $c$ (differing by $\pi$) for four different excitation spectra: the experimental (figure 2(a)), a square-shaped (figure 2(d)), a Gaussian-shaped (figure 2(g)) and a mixture between one-third squared-shaped with two-third Gaussian-shaped (figure 2(j)), which simulates the experimental spectrum (figure 2(a)). The simulation is based upon classically described electric fields, disregarding any interaction with matter. For a simulated Gaussian spectrum (figure 2(g)), the modulation amplitude is almost negligible for an interpulse spacing over one full-width at half-maximum (FWHM). However, for real pulses, which usually differ from a Gaussian envelope by smaller wings, the modulation of the multipulse sequence’s envelope can be considerable. The small but non-negligible temporal wings due to the non-Gaussian envelope of the experimental spectrum lead to a significant $c$-dependent sub-pulse modulation. This can dramatically be seen when a squared-shaped spectrum is assumed: figures 2(e) and (f)
Figure 3. Sub-pulse interference effect explaining transient absorption data in the SW. (a) Dependence of the sub-pulse amplitude modulation on parameter $c$ for the calculated two-component spectrum (solid line) and the TA signal at the respective probe delay (squares) ($b = 56$ fs). (b) Maximum $c$-induced modulation of the amplitude of sub-pulse at $56$ fs for different values of the interpulse interval $b$.

show a strong modulation of the sub-pulses intensity, which is a direct consequence of the interference between the sub-pulses. By varying the parameter $c$, the relative phase between the sub-pulses is modified and consequently the interference also changes. That leads to different excitation intensities for each sub-pulse depending on parameter $c$ and therefore to the modification observed in figure 1(b). It is important to note that this modification of the excitation envelope is a major contribution to the strong signal oscillations observed inside the SW. It has to be distinguished from molecular phenomena like wavepacket motion.

To validate the importance of this field-only effect, the MEM’s magnitude for the two-component spectrum was compared with the transient absorption data from Nile Blue for a sub-pulse spacing of 56 fs. Figure 3(a) shows the variation of the transient absorption signal at delay 56 fs (see figure 1(a)). A strong modulation of about 40% can be observed. The simulation of the MEM effect (solid line) nicely matches the TA experimental behaviour. The good agreement with the experimental data also shows that, in the case of a multipulse sequence generated with a sinusoidal phase function, the optical sub-pulse interference effect poses an additional but decisive contribution to the molecular transients in the SW. However, it
is important to note that for other probe delays e.g. $\tau = 0$ fs (figure 1(b)), the signal still shows $c$-dependent oscillations. They are not easily disected due to the strong overlap oscillations due to molecular vibrations. Recalling the discussion of figure 2, the degree of ‘squareness’ in the experimental spectrum is responsible for the observed MEM. As a consequence, this effect is strongly dependent on the sub-pulse spacing $b$ because this parameter defines the temporal spacing and, as a result, the temporal overlap between the sub-pulses (figure 3(b)). The amplitude in this figure describes the maximum $c$-induced variation of the intensity of the sub-pulse at 56 fs. This figure gives the degree of MEM effect for a given sub-pulse separation. The modulation is still present even for separations larger than 4 times the FWHM of the Fourier-limited duration of 20 fs, namely 80 fs in this case, but it becomes negligible when the pulses within the sequence are separated by an amount larger than five FWHM in our case (figure 3(b)).

The interpulse interference effect might have important consequences for the interpretation of pump–probe experiments with phase-tailored excitation because the $c$-dependent modulation of the sub-pulse’s amplitude influences the transient signal at early delay times in an unanticipated manner: the modulation within the SW is neither exclusively defined by the excitation pulse form nor relates to any material dynamics only.

Even though the molecular dynamics inside the SW are congested with optical effects, the analysis at these early delay times can still be performed. One method is the calculation of the transient signal taking in account coherent and sequential transient contributions after the tailored excitation [39, 40]. This can be very time consuming and depending on the degrees of freedom of the system (e.g. number of electronic states and vibrational modes) not easily tractable. Under the experimental conditions of this work, coherent contributions, like coherence spikes due to two-photon absorption, stimulated Raman amplification or cross-phase modulation [45], play only a minor role and can be ignored. Sequential contributions, like population and vibrational dynamics, can be distinguished from the MEM when the phase of the excitation pulse is cycled. In practical terms, this means to average the residuals transients from $c = 0$ to $2\pi$ inside the SW, resulting in a molecular transient free of any shaping interference effect (figure 4(b)). Similar phase-cycling schemes were already employed successfully in two-dimensional spectroscopy to select desired femtosecond structural dynamics [46, 47].

The findings discussed here imply important consequences for closed loop coherent control experiments, where the retrieved optimal pulse shape resembles a multipulse sequence. Such control schemes were particularly exploited with success for control of the photophysics of biomolecules [7, 19, 21, 48]. Due to the adaptive approach that the optimal pulses are generated, the MEM effect inside the SW can be much more striking in closed loop experiments. In this case, contrasting to the sinusoidal phase function used here, multipulse sequences are very often made of different sub-pulses intervals with different amplitudes and widths. Under the light of the data presented here, simplistic analysis of the modulations in the transient absorption signal within the SW must be carefully performed, since the oscillatory contribution is most likely due to MEM. If molecular dynamics is expected within the SW, replacing the closed loop result with an according sine-phased-modulated multipulse and then cycling the phase, may help to elucidate whether the coherent control mechanism relates to modulation of wavepackets or to a mere optical artefact. The parameterization of closed loop results with more physically intuitive phases can be of great help in this regard and was already demonstrated in experiments of different complexity [7, 19, 24, 31].

Effects of interpulse interferences due to multipulse shaping are a general result and are not limited to transient absorption measurements but are also to be carefully considered in other
Figure 4. Phase-cycling for extracting the molecular dynamics. (a) The residual TA signal after the subtraction of the slow population dynamics is shown for two multipulse sequences with the parameter $c$ differing by $\pi$ (open and full circles, respectively). Repeated from figure 1 for comparison. (b) The average of the residual of all transients of figure 1(b) gives a molecular vibrational dynamics free of any multipulse interference effect.

nonlinear time-resolved techniques, such as four-wave mixing experiments [49, 50]. Techniques based on tailored single-beam excitation are also under effect of similar interferences, which can be also filtered out by scanning the phase of the excitation pulse [14]. In general, for phase-only control experiments, special care has to be taken when contrasting transients after optimal and anti-optimal excitation pulses. The respective alteration in pump–probe signals might be attributable to MEM and not to different molecular dynamics for optimal or anti-optimal pulses.

Finally, it is important to note that the MEM effect is mostly important for non-Gaussian-shaped excitation spectra, which is true in many circumstances for ultrashort pulses. In this case, in order to avoid any MEM, a sub-pulse temporal separation larger than five times the FWHM is required. When the excitation pulses are short enough ($<20$ fs), this poses of course no restriction for the control of low-frequency vibrational wavepackets, which requires accordingly long sub-pulse separations, but it may be challenging in the case of high-frequency wavepackets. In this situation, a way to circumvent this problem is to use a larger temporal spacing between the sub-pulses, which is an integer multiple of the molecular wavepacket period [17], provided that the molecular dynamics and coherence times last long enough [18]. If on the other side, the molecular sample does not present a closed system, meaning that during the excitation time a strong coupling to other modes or relaxation into a bath takes place, the $c$-dependence might indeed have an effect on the molecular dynamics. In that case, the phase-cycling may
not be used straightforwardly because it will also average the $c$-dependent molecular signal. Molecular $c$-dependent effects on the SW are an important control mechanism of population and vibrational coherence excitation but which was found to play a minor role in the case of Nile Blue. Such effects will be discussed thoroughly in future in another contribution. Nevertheless, if the objective is to control a specific outcome, which is detected for example after the SW, the MEM then does not affect the interpretation of the coherent control result.

4. Conclusions

Ultrafast spectroscopy with tailored pulse sequences is an important and powerful technique with widespread applications in particular for analysing complex dynamics in biological systems. In the field of quantum control spectroscopy (QCS) [7, 20], [51]–[53], where molecular dynamics after Fourier-limited excitation are compared with the system’s evolution after a phase-modulated actinic pulse, new conclusions inaccessible by conventional spectroscopy can be drawn. In this paper, we discussed an important interpulse interference effect related to multipulses, which can be erroneously taken as molecular dynamics in time-resolved experiments. The phase of the multipulse is responsible for a modulation in the transient signal similar to molecular oscillations. It turns out that the spectral shape of the excitation pulse is very important for the observation of the effect, which ideally should have a Gaussian shape. Nonetheless, when the phase factor is scanned, this effect can be exploited to readily deliver information on molecular dynamics free of optical artefacts throughout the entire region of the transient.

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