Pulse trains in molecular dynamics and coherent spectroscopy: a theoretical study

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Abstract. Pulse trains (PTs) generated by sinusoidal phase masks emerged as a popular tool in the field of coherent control and have been applied successfully in many experiments. Although many attempts were made to throw light on the mechanism of the induced processes, it is not yet fully understood. Based on nonperturbative quantum dynamical calculations in the grid representation, we will elucidate the mechanism of PT excitation between anharmonic bound molecular electronic states. We extract general rules for the prediction of induced dynamics and the resulting spectra. The results allow us to outline perspectives for new applications, especially in the field of nonlinear spectroscopy.

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1. Introduction

The field of coherent control initially aimed at the steering of chemical processes has today emerged in many research directions ranging from quantum optics to biology [1]–[12]. Prominent examples in life sciences are the manipulation of energy transfer in the light-harvesting complex, an active part in photosynthesis [13], or the isomerization of retinal, part of the vision process [14]. Aspects of coherent control also entered into nonlinear spectroscopy [15]–[18]. One common feature in both areas is the application of pulse sequences [19], where the phase relation between individual subpulses as an additional control variable was introduced by shaping technologies [4], [20]–[23]. In nonlinear spectroscopy, in analogy to nuclear magnetic resonance (NMR), many experiments are performed using sequences of pulses to extract information of the system response profiting from interference effects [24, 25]. Especially, optical two-dimensional (2D) spectroscopy relies on the Fourier transformation to extract the information encoded in the phases of interacting light pulses [21], [26]–[28].

The early success achieved by applying pulse trains (PTs) of randomly distributed phases to control coherent phonons in a crystal [29] was later improved by the use of spatiotemporal pulse shaping [30]. Recently, chirality-selective excitation in carbon nano-tubes could be realized [31]. Rotational modes could be controlled theoretically by the application of PTs [32, 33]. PTs consisting of several pulses also emerged as a fundamental pattern in experimentally optimized pulse fields driving molecular processes [13, 14, 34].

Specific PTs with a defined phase relation are experimentally easily generated by phase modulation applying a sinusoidal mask function. The complete PT is then characterized by only three parameters: the amplitude, the interpulse distance and the phase relation between the single subpulses. This parameterization allows for systematic investigation and interpretation of control results and turned PTs into a popular tool for control experiments [35]–[38]. Successful demonstration reported the control of enhancement or even the depletion of vibrational modes [39]–[41]. Further experiments realized the control of molecular state population [38], [42]–[44]. The control of population transfer with PTs was also studied theoretically, either with the aim of chemical reaction control [45, 46] or in the scope of quantum information [47]. Possible mechanisms of PT excitation were discussed in the literature. Subpulses enhancing the excitation of degrees of freedom by repeatedly driving the system like pushing a child at the swing were proposed [29], but at the same time challenged to be rather a macroscopic than a quantum effect [48]. Although many attempts have been made to decipher the induced mechanism, it was not yet possible to explain all the observed effects when multilevel systems are involved. In the present work, we investigate trains of multiple subpulses generated by sinusoidal mask functions for electronic excitation. Based on systematic quantum dynamical investigations, we elucidate the induced mechanism, connect the different perspectives of PT excitation with respect to dynamics and spectroscopy, and provide rules for future spectroscopic applications.

This paper is structured as follows: in section 2, we introduce the model system, the dynamics induced by Fourier-limited (FL) ultrashort pulses and the link to experimentally obtainable spectra. PTs and their parameters of interest are introduced in section 3. After a short demonstration of possible PT effects in section 4, we systematically investigate the influence of the pulse parameters for the selected model system and derive some general rules for PT excitation. In section 5.1, we draw the connection to FL pulse excitation, interpret
the obtained results and show their relevance for experimental observations. In section 5.2, we derive an analytic expression based on perturbation theory to explain and quantify the PT-induced mechanism. Finally, in section 6, we summarize our findings and show perspectives for the possible future application of PTs in nonlinear spectroscopy.

2. The model system

The quantum dynamics of light–molecule interaction are simulated by solving the time-dependent Schrödinger equation (TDSE):

\[
\Psi(t) = -i H \Psi(t) = -i \begin{pmatrix} T + V_g(x) & \epsilon(t) \mu(x) \\ \epsilon(t) \mu(x) & T + V_e(x) \end{pmatrix} \begin{pmatrix} \Psi_g \\ \Psi_e \end{pmatrix}
\]

(1)

with \( T \) the kinetic Hamiltonian, \( V_g \) and \( V_e \) the potential energy surfaces of the electronic ground and excited state, \( \mu \) the electronic transition dipole moment and \( \epsilon(t) \) the time-dependent laser field. The grid wave functions \( \Psi_g \) and \( \Psi_e \), by transformation to the eigenstate basis, can be represented as superpositions of vibrational eigenstates \( \phi_{i,n} \) in the electronic ground and excited state. Their complex time-dependent coefficients \( c_{i,n}(t) = |c_{i,n}| e^{-i\omega_{i,n} t} \) rotate in the complex plane according to their individual vibrational eigenfrequencies \( \omega_{i,n} \):

\[
\Psi_i(t) = \sum_n c_{i,n}(t) \phi_{i,n}.
\]

(2)

The evolution of wave packets (WPs) \( \Psi_i \) is characterized by the population of the vibrational states \( |c_{i,n}| \) and by the phase differences \( \Delta \omega_{i,j} \) between them.

To study the mechanism of electronic PT excitation in multilevel systems, we set up a 1D model of two optically coupled electronic states with the shape of a Morse potential

\[
V_{\text{Morse}} = D \left( 1 - e^{-\alpha (x-x_0)} \right)^2
\]

(3)

with the asymmetric parameter \( \alpha = \alpha_0 \sqrt{m/2} \), the frequency \( \omega = 178 \text{ cm}^{-1} \), the mass \( m = 4450.6 \text{ au} \) (4.0542 \( m^{-27} \text{ kg} \)) and the dissociation energy \( D = 152 \text{ nm} \). The two electronic states are energetically shifted about \( \Delta \epsilon(e,g) = 506 \text{ nm} \) and displaced along \( x \) about \( x_0 = 1.5 \text{ au} \) (\( 7.9377e^{-11} \text{ m} \)) (figure 1). The parameters are taken from our model system of the coupled dynamics of \( \beta \)-carotene, studied in [49].

As reference for our PT studies, in the present section, we introduce the dynamics induced by an unshaped FL pulse of a full width at half maximum (FWHM, respectively the field amplitude) of 16 fs, center frequency \( \omega_0 = 20,648 \text{ cm}^{-1} \) and a maximum amplitude of 0.0034 \( \text{ GV cm}^{-1} \). The FL pulse transfers about 4\% of population to the electronically excited state \( V_e \) (cf figure 2) and generates a WP with a Gaussian distribution in \( V_e \) covering several vibrational levels with a maximum at the fourth vibrational level (figure 3).

After laser excitation, the system evolves under the influence of the unperturbed system Hamiltonian, meaning the coefficients \( c_n \) rotate in the complex plane with the vibrational eigenfrequencies (cf equation (2)).

The excited WP \( \langle \psi_e(t) | \psi_e(t) \rangle \) oscillates in the potential \( V_e \) with the classical period \( T_{cl} \approx \frac{2 \pi}{\omega} \approx 186 \text{ fs} \) (figure 4).

In the Wigner representation of the WP (equation (4), where \( x = q + \frac{s}{2} \) and \( x' = q - \frac{s}{2} \)),

\[
f_W(p, q) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i p (x-x')} \langle x' | \psi \rangle \langle \psi | x \rangle \, ds,
\]

(4)

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Figure 1. Potential energy surfaces of the model system. The blue arrow indicates laser excitation between the electronic ground state \( V_g \) and the electronic excited state \( V_e \).

Figure 2. Transfer of electronic population to the electronic excited state \( V_e \) by an FL pulse of \( \omega_0 = 20648 \text{ cm}^{-1} \) and FWHM = 16 fs.

the WP rotates in phase space (cf figure 5). The small deviation from a state of minimal uncertainty indicates the evanescent phase difference \( (\Delta \phi_{i,j} \approx 0) \) between the vibrational modes.

The excited state WP dynamics can be traced in the square of the time-dependent autocorrelation function (TDCF) \( |C(t)|^2 \):

\[
|C(t)|^2 = |\langle \psi_g(t_0) | \psi_e(t) \rangle|^2, \\
= \sum_{i,j} 2|\gamma_i||\gamma_j| \cos ((\omega_i - \omega_j)t + \Delta \phi_{i,j})
\]
Figure 3. Formation of a WP in $V_e$ using an FL pulse of FWHM of 16 fs. Due to the local displacement between the two electronic states, the FC factors, defined as the overlap $\langle \phi_{g,0} | \phi_{e,n} \rangle$, together with the Gaussian shape of the laser pulse, lead to a Gaussian distribution over the vibrational states, with its maximum at $n = 4$.

Figure 4. Oscillation of the excited WP $\langle \psi_e(t) | \psi_e(t) \rangle$ after FL excitation in $V_e$ with the period of $T_{cl} = 186$ fs.

with $\gamma_i = (\langle \phi_{g,0} | \phi_{e,i} \rangle)^2$, and is related to the experimentally obtainable transient pump probe spectra [50]. Figure 6 (top) shows the results of the TDCF after FL excitation during the first 1.2 ps. The temporal oscillation of the overlap between the prepared and the initial ground state clearly reflects the oscillation period of $T_{cl} = 186$ fs.

By Fourier transformation of $|C(t)|^2$, we obtain the corresponding frequency spectrum $\sigma(\omega)$ (figure 6, bottom). It shows the frequency differences of the individual WP components, i.e. the coherences of the prepared state,

$$\sigma(\omega) = \sum_{i,j} |\gamma_i| |\gamma_j| \delta(\omega_i - \omega_j),$$

and is related to the results obtained from nonlinear spectroscopy. The fundamental transition located at 179 cm$^{-1}$ is due to the one-quantum coherences. The multiquantum coherences,
Figure 5. Snapshots of the Wigner representation of the excited state WP after FL excitation during the first oscillation period. The circular shape reflects the concerted phases of the vibrational levels. The WP rotates in phase space with the period of $T_{ci} = 186$ fs.

Figure 6. Correlation functions of the excited state WP. Top: the TDCF $|C(t)|^2$ of the excited state WP after FL excitation during the first 1.2 ps. Bottom: the correlation function in frequency domain $\sigma(\omega)$ shows the coherences $\Delta\omega_{i,j}$ of the observed WP, the fundamental (179 cm$^{-1}$) and the higher harmonics.

respectively the higher harmonics, are observed with decreasing intensities. Due to the short recording time of 1.2 ps, the resolution is not sufficient to resolve the anharmonicities of the present system.

3. The PT

The PTs studied in the present work are experimentally generated from FL pulses $\epsilon_{FL}(t) = Ae^{-(t-t_0)/\sigma^2}\cos\omega_0(t-t_0)$ by application of a sinusoidal parameterized mask function $\Phi_M(\omega) = a \sin (b\omega + c)$ [36]. The three parameters $a$, $b$ and $c$ denote the amplitude of the phase
modulation, the frequency of the sinusoidal oscillation and an absolute phase offset. Using the Jacobi–Anger identity
\[
e^{i\omega \sin(\xi)} = \sum_{n=-\infty}^{\infty} J_n(a) e^{in\xi},
\]
where \(J_n\) denote Bessel functions of the first kind, the spectrum of the modulated pulse in the frequency domain,
\[
\epsilon_{\text{PT}}(\omega) = \epsilon_{\text{FL}}(\omega) e^{i\Phi_M(\omega)},
\]
can be expressed in the time domain as
\[
\epsilon_{\text{PT}}(t) = e^{i\omega_0 t} \sum_{n=-\infty}^{\infty} J_n(a) \epsilon_{\text{FL}}(t + nb) e^{inc}.
\]

In the present study, all PTs are generated using equation (10) and the FL pulse \(\epsilon_{\text{FL}}(\omega)\), characterized in section 2. Their electric fields are directly comparable with the experimental ones generated by application of a phase mask \(\Phi_M(\omega)\) with \(a = 1.23\), leading to a train of 5 subpulses and a total energy equal to that of the unshaped field. In figure 7, we demonstrate the effect of the parameter \(c\) for PTs with \(b\) exceeding the width of the unshaped pulse. For illustration of the phase relation \(\omega_0\) is reduced to obtain a few cycle pulses. The individual subpulses are phase-shifted replicas of the unshaped FL field, only differing in amplitude. The nearly Gaussian amplitude distribution is caused by the choice of \(a = 1.23\) and can be deduced from the Bessel functions of equation (10). The subpulses are separated in time by the interpulse distance \(b\) and have a distinct phase relation \(c\). The carrier envelope phase of the PT is chosen such that the phase \(\phi\) of the central subpulse is zero. Subpulses preceding the central one have phase differences of \(\Delta\phi = c\) to their next neighbor, while subsequent subpulses have phase differences of \(\Delta\phi = \pi - c\).

4. Phenomenological investigation of PT excitation

4.1. General PT effects

To obtain first insights into the effects induced by PTs, we solve equation (1) with the PT introduced in section 3 (equation (10)) and vary the two pulse parameters, the interpulse distance \(b\) and the phase \(c\), of the fields introduced. The results will be discussed in comparison with the FL pulse excitation, presented in section 2.

For the first three subpulses, we observe a population transfer from the electronic ground state to the excited state (figure 8). The following subpulses either continue the population transfer or depopulate, depending on the choice of \(b\) and \(c\). The effect of the phase parameter \(c\) is strongly correlated to the choice of the interpulse distance \(b\). The amount of population in the excited state after the PT varies within 20% for different \(b\) and \(c\) values. Although the PTs are of equal energy, only 5% of the total amount of the FL case is transferred.

For more detailed information, we follow the population pattern on the level of the vibrational eigenstates (figure 9). The individual vibrational levels are affected in a much more complex way by the subpulses, highlighting the importance of multilevel systems for the analysis of PT excitation [52]. Already the second subpulse can cause strong deviations from the FL excitation (figure 3). Depending on the choice of \(b\) and \(c\), at a first glance without
Figure 7. Model PT in the time domain; $\omega_0$ is reduced to accentuate the subpulse phases. By the use of the phase mask $\Phi_M(\omega) = a \sin(b\omega + c)$, a train of FL subpulses is generated. The amplitude and the number of subpulses are caused by the choice of the amplitude $a$ (here $a = 1.23$) and the interpulse distance is defined by $b$. The parameter $c$ defines the phase relation between the subpulses. The carrier envelope phase of the PT is chosen such that the phase $\phi$ of the central subpulse is zero. The phase difference between adjacent subpulses preceding the central one is $\Delta\phi = c$, while adjacent succeeding subpulses differ in phase by about $\Delta\phi = \pi - c$.

any systematics, in some levels Rabi oscillation during subpulses can be observed. Due to Rabi cycling, a part of the pulse energy is used to deexcite the electronic population. This explains the strong differences between the amount of electronic state population after the PT in comparison to the FL case. We also observe a deviation from the Gaussian distribution over the vibrational states during the PT.

Not only the population, but also the evolution of the induced excited state WP differs strongly with the pulse parameters. The effect of the interpulse distance $b$ was seen to be

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Figure 8. Population transfer to the electronic state $e$ induced by PT (sketched in black). The process is strongly influenced by the choice of the interpulse distance $b$ and the phase $c$. Subpulses following the central one show major sensitivity to the two pulse parameters and can even invert the transfer direction.

In figure 10, the WP evolutions for different $b$ values are shown. The induced dynamics manifests itself in a regular pattern of differing complexity due to interference effects. The structure and characteristics of such space–time evolutions of the WP, also known as quantum carpets, have been studied before in many systems theoretically [53]. The structure of a quantum carpet similar to that in figure 10, bottom, was theoretically predicted to appear in pump–probe experiments [54] and was subsequently experimentally observed [55]. In general, interference effects between WPs and subpulses are an established phenomenon. In the field of WP interferometry, the control of these effects, among others, aims to obtain spectroscopical information [56, 57]. With decreasing $b$ values the pattern becomes increasingly complex and hard to interpret. For this reason, we will switch to phase space.

In Wigner representation (figure 11), WP evolution after PT interaction also differs significantly from that obtained by the unshaped pulse. Again the influence of $b$ predominantly
Figure 9. The effect on vibrational populations strongly differs by variation of the two PT parameters \( b \) and \( c \). The single vibrational levels are affected individually by each subpulse, revealing the importance of consideration of a multilevel system to decipher the induced mechanism.

determines the structure in phase space. In almost all cases, the WP has spread, contrary to the FL case (figure 5), indicating that the vibrational levels changed their relative position in phase space. Depending on \( b \) we observe a complex pattern, in some cases still preserving some kind of symmetry. All these structures fulfill a rotation in phase space with the period \( T_{cl} \).

The Fourier transform spectra (figure 12) of the correlation functions after PT excitation also differ from the spectrum obtained by FL excitation. Depending on parameters \( b \) and \( c \), the peak amplitudes are reduced. We even observe the disappearance of individual peaks, an effect that coincides with the observations made in several control experiments using sinusoidally shaped PTs on molecular systems [35], [39]–[41].
Figure 10. The dynamics of the WP induced by PT (PTs are sketched in black, including the phase jump between subpulses three and four) strongly differs from the dynamics after FL excitation (cf figure 4). Each subpulse generates a sub WP, leading to complex interference patterns also called quantum carpets.

4.2. Systematic investigation of \( b \) and \( c \)

To understand the PT effects introduced in section 4.1, we will systematically analyze their relation to pulse parameters \( b \) and \( c \) taking as reference the results from the FL pulse in section 2.

First, we examine their dependence on the interpulse distance \( b \). The variation in \( b \) is set in relation to the oscillation period \( T_{cl} \) of our system and the parameter \( c \) is kept constant \( (c = 0) \).

In figure 13, the time-dependent population of the vibrational levels for \( b = T/2 = 93 \text{ fs} \) (top) and \( b = T/3 = 62 \text{ fs} \) (bottom) is shown. The effect of the first subpulse is the same as for the FL excitation, forming an excited state WP with a Gaussian distribution of vibrational levels. The characteristics of the following subpulses control the intermediate and final temporal and spectral pattern.

When \( b \) is set to half the oscillation period \( T_{cl} \), we observe that even and odd levels are populated alternatively by the following subpulses, leading to an alternating distribution over
Figure 11. Snapshots of phase space structures induced by PTs. The shape of the structures primarily depends on the choice of the interpulse distance $b$. Like the FL-induced Wigner WP (cf figure 5), they rotate in phase space with $T_{cl}$. In some cases, the structures tend to have an $n$-fold symmetry.

Figure 12. Spectra obtained after PT excitation for different $b$ and $c$ values. The same frequencies are observed as in the FL spectrum (black dashed line, cf 6), but the intensity of single peaks is varied depending on $b$ and $c$. Some peaks even disappear.

the vibrational levels after the second and the third subpulses. The original Gaussian distribution after the first subpulse is now separated in a Gaussian distribution over odd and one over even levels. In the present case, the even levels are dominant, i.e. more populated. The fourth and fifth subpulses reverse the described separation, reinstalling in the end an almost balanced Gaussian distribution, with its maximum in the fourth vibrational level after FL excitation.

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Figure 13. Selective population of vibrational levels in dependence of $b$. Top: for $b = T_{cl}/2$ vibrational levels of the same residue classes mod.2 show similar excitation behavior. The dominant population of even levels during the first half of the PT is reversed by the last two subpulses. Bottom: for $b = T_{cl}/3$ vibrational levels of the same residue classes mod.3 show similar excitation behavior.

When $b$ is set to a third of $T_{cl}$ (figure 13, bottom), we observe comparable behavior, except for a threefold separation. To classify this behavior, we introduce a congruence relation on the vibrational levels, defining residue classes modulo $\alpha$ ($\gamma \mod \alpha$, $\alpha \in \mathbb{N}$, $\gamma \in \{0, 1, \ldots, (\alpha - 1)\}$) as the sets of vibrational levels $v_n$, that leave the same remainder $\gamma$ when the quantum number $n$ is divided by the modulus $\alpha$. We observe that vibrational levels of the same residue classes mod.3 are affected similarly by the subpulses. Again the induced separation is reversed by the last two pulses, leaving at the end again a nearly Gaussian distribution around $v_4$.

The corresponding WP dynamics are presented in figure 10, middle ($b = 62 \text{ fs} = T/3$) and bottom ($b = 93 \text{ fs} = T/2$). As in the FL case, the first subpulse induces a WP in the Franck–Condon (FC) region of the excited state, which starts to oscillate with the usual period of $T_{cl} = 186 \text{ fs}$. For the $b = T/2 = 93 \text{ fs}$ case, the second pulse creates a second WP when the first WP has reached the outer turning point. The following subpulses will always coincide with the already induced WPs localizing in the FC region and only change their intensities. Finally, a state is created constituted of two sub-WPs counter-oscillating in the potential and inducing an interference pattern in the middle of the potential when they cross.
When $b = T/3 = 62 \text{ fs}$, we observe a similar behavior. Only this time three sub-WPs are induced by the first three pulses, again counter-oscillating in the potential with $T_{cl}$. The interference pattern now appears in each third of the potential, originating from the crossing of two of the three WPs. The resulting structure is already complex, making it hard to discriminate between individual WPs.

The picture becomes clearer in the Wigner representation. For $b = T/2$, we observe a phase space structure of twofold symmetry rotating with $T_{cl}$ (figure 11, left bottom). We can assign the two outer maxima to the two WPs prepared and the central structure to the interference pattern induced. Accordingly, the Wigner representation for $b = T/3$ shows a threefold symmetry (figure 11, right top). In principle, this behavior can be systematically extended to $b = \frac{\beta}{\alpha} T$, ($\alpha, \beta \in \mathbb{N}$), provided that the number of subpulses as well as the number of vibrational levels involved are sufficient to resolve the interference pattern.

We notice that in phase space it is easier to distinguish between the single WPs, which are the circles in the outer sphere of the structure, while the patterns in between arise due to interference.

The observations described can be extended to $b$ values as arbitrary fractions of $T_{cl}$ and can be summarized, for $b = \frac{\beta}{\alpha} T$:

- Variation of the subpulse distance $b$ leads to a selective addressing of vibrational levels of residue classes modulo $\alpha$ and an intermediate selective population according to these classes.
- Except for a slight deviation, the Gaussian distribution is restored at the end of the PT.
- If $\alpha$ is small enough, a number of $\alpha$ distinguishable sub-WPs, phase shifted by about $\Delta \varphi = 2\pi \frac{\beta}{\alpha}$, are created by the PT, resulting in a state with an $\alpha$-fold symmetry axis in phase space.

Changing also the parameter $c$ reveals a clear correlation with the selected $b$ values. In figure 14, we show the evolution of the electronically excited state population during the PT for $c$ values in the range of $[0; 2\pi]$ and for $b$ values of $1/3T$, $1/2T$ and $1T$. The $c$ effect can be interpreted as an interference effect between already induced sub-WPs and subpulses in the FC region. The first subpulse that coincides with a previously generated WP creates an electronic population oscillating along $c$ with a periodicity of $b$. Subpulses not synchronized with the WP motion show no distinguishable $c$ effects. The oscillations along $c$ become more complex if a sub-WP interferes twice with a subpulse.

The $c$ dependence of the population of the vibrational levels (figure 15) shows a division in $\alpha$ classes during the first half of the PT. For $b = T_{cl}/2$ and $c$ varying in the range of $[0; 2\pi]$ (figure 15, right), we observe antiparallel behavior for gerade and ungerade levels. The similar behavior of $v_2$ and $v_4$ is clearly seen and is the same for all other gerade levels. When $b = T_{cl}/3$ (figure 15, left), three classes with respect to $c$ can be distinguished. By the choice of $c$ it is possible to select the residue class, which is predominantly excited in the first half of the PT, or reach a balanced population of residue classes. By the following subpulses the difference in population of the residue classes is almost compensated.

For selected values of $c$, we also show the WPs for $b = T_{cl}/2$ and $b = T_{cl}/3$ in the Wigner representation (figure 16). Variation of $c$ disturbs the symmetry of the phase space structures obtained by variation of $b$. In both examples, two of the sub-WPs exchange intensity. Symmetric structures appear where all of the induced WPs have nearly the same intensity and distorted
Figure 14. Evolution of the electronically excited state population $\langle \Psi_e \rangle$ during the PT for $c$ values in the range of $[0; 2\pi]$ and for $b$ values of $1/3T$, $1/2T$ and $1T$. Individual $c$ slices of these figures have already been shown in figure 8, and revealed a strong dependence of $\langle \Psi_e \rangle$ on the two parameters $b$ and $c$. Oscillations along $c$ with a periodicity of $b$ occur, when a subpulse interacts with an already induced WP. Repeated subpulse interaction induces a more irregular oscillatory pattern.

symmetries, where one of the two interacting sub-WPs vanishes. These features should be experimentally observable in the FT spectrum.

In figure 16, we added the corresponding spectra, recorded after pulse excitation. For symmetric phase space structure, the frequencies of the fundamental and some higher coherences vanish in the spectra. Asymmetric phase space structures result only in an amplitude damping of these frequencies. The Fourier-transformed spectrum $\sigma(\omega)$ displayed as a function of $c$ for $b = T_{cl}/2$ and $b = T_{cl}/3$ (figure 17) shows peaks oscillating with a period of $2\alpha$ and peaks of constant amplitude. With slight modifications of $b$ this oscillation shifts along the $c$-axis.

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To sum up the $c$ effects observed:

- $c$ determines which of the vibrational residue classes $\text{mod.} \alpha$ has intermediate dominance;
- the precise $c$ value for selection of a dominant residue class sensitively depends on $\alpha$;
- $c$ determines the regularity of the $\alpha$-fold symmetry in phase space;
- symmetric phase space structures are obtained by $c$ values inducing a balanced population of the residue classes during the first half of the PT;
- $c$ determines the amplitude of specific peaks in the spectra, preselected by $\alpha$;
- complete annihilation of peaks is reached only by symmetric phase space structures.

5. Analytical derivation of the PT mechanism

In the previous sections, we worked out more general rules predicting the outcome of PT excitation with respect to the vibrational populations, the resulting structures in phase space and the related frequency spectra, when the interpulse distance $b$ and the phase $c$ are varied. To verify
Figure 16. Snapshots of the prepared states after PT excitation in phase space and the resulting spectra in the frequency domain. Parameter $c$ decides whether a created state is symmetric or not. Symmetric states have damped amplitudes of frequencies of the different coherences, depending on the symmetry axis.

our observations and underline their predictive power, we will derive analytical expressions for PT excitation.

5.1. Long-time dynamics in an anharmonic potential

We start with a brief review characterizing the key elements of WP dynamics in anharmonic systems [58]–[60]. For a Gaussian-type WP, centered around a vibrational level $\tilde{n}$, like prepared
Figure 17.  

$c$ dependence of the frequencies after PT excitation with $b = 93\, \text{fs} = T_{\text{cl}}/2$ and $b = 62\, \text{fs} = T_{\text{cl}}/3$. We observe an oscillatory behavior of peak amplitudes preselected by the choice of $b$, with a period of $2\alpha$ ($\alpha = 2, 3$).

by FL excitation (cf equation (2)), the frequencies of the anharmonic system can be expanded in a Taylor series of the vibrational quantum number around $\bar{n}$,

$$
\omega(n) = \omega_{\bar{n}} + \left( \frac{\partial \omega}{\partial n} \right)_{\bar{n}} (n - \bar{n}) + \frac{1}{2} \left( \frac{\partial^2 \omega}{\partial n^2} \right)_{\bar{n}} (n - \bar{n})^2 + \cdots.
$$

(11)

The classical oscillation time

$$
T_{\text{cl}} = \frac{2\pi}{\left| \left( \frac{\partial \omega}{\partial n} \right)_{\bar{n}} \right|}
$$

(12)

is given by the linear term of equation (11). Due to the anharmonicity of the system additional timescales arise through the higher order terms. We will consider up to second-order effects, thus including the revival time

$$
T_{\text{rev}} = \frac{2\pi}{\frac{1}{2} \left| \left( \frac{\partial^2 \omega}{\partial n^2} \right)_{\bar{n}} \right|}.
$$

(13)

The different timescales are observable in the TDCF of WP evolution (cf $T_{\text{cl}}$: figure 6, top and $T_{\text{rev}}$: figure 18, top) [58].

The reversible de- and rephasing of WP components due to anharmonicity is mirrored by the decay and revival of $|C(t)|^2$. The complete and partially rephased states manifest themselves
The TDCF of the FL excited state in the picosecond regime shows collapses and revivals originating from the reversible de- and rephasing of the anharmonic levels. The partially rephased states, called fractional revival states, show symmetric phase space structures similar to those obtained by PT excitation of appropriate $b$ and $c$.

As global and local maxima. The characteristics of these full and fractional revival states can be traced out by substitution of equation (11) into equation (2) and replacing the time by the individual recurrence time $t_{R} = \frac{B}{2A} T_{rev}$, with $A, B \in \mathbb{N}$:

$$\Psi_{i}(t) = \sum_{n} |c_{i,n}| \exp \left[ -i \left( \frac{2\pi}{T_{cl}} (n - \tilde{n}) + \frac{2\pi}{T_{rev}} (n - \tilde{n})^2 \right) \frac{B}{2A} T_{rev} \right] \phi_{i,n}. \quad (14)$$

Considering the exponent, at a fractional revival of $t_{R}$, the vibrational levels of the WP are, with respect to their difference from $\tilde{n}$, separated in the residue classes of $A$ with equal phase factors. The phases of these classes differ by about $\Delta \varphi = 2\pi \frac{B}{A}$.

In the evolution of the FL excited WP in Wigner representation, where this dephasing and partial rephasing are illustrated very clearly (cf figure 18, bottom), we find similar structures as previously discussed for the PT excitation. In the snapshot of the FL excited WP at 21 ps, a collapsed state, spread over the complete phase space, is shown. At fractional revival times $t_{R}$ we observe the formation of $A$ sub-WPs, each one phase shifted by about ($\frac{2\pi}{A}$) from its neighbor. Together with the corresponding interference pattern an $A$-fold symmetry is formed, similar to the one obtained for PT excitation with $b = (\frac{1}{a} T_{cl})$ (cf section 4).

With the help of a sliding window Fourier transform of the TDCF,

$$S(\omega, \tau) = \int_{0}^{\infty} S(t) g(t - \tau) e^{-i\omega t} dt, \quad (15)$$

the time dependence of the spectral contributions can be resolved (cf figure 19, bottom), also experimentally [61]. At fractional revival times, due to the interference of phase-shifted
sub-WPs, individual peaks in the spectra are suppressed. At full and fractional revivals the WP is localized again and all frequency peaks appear in the spectra. At revival times $t_R, A = 1, 2, 3$ (figure 19, top), we observe the same features as previously generated by PT excitation for $\alpha = 1, 2, 3$ (cf figure 16). Obviously, the phase differences $\Delta \varphi_{i,j}$ (equation (6)) in the initially prepared Gaussian WP with respect to the window used in equation (15) have separated in the individual residue classes. From this comparison it becomes clear that the loss of amplitudes in the FL as well as PT spectra results from an interference of the coherences of phase-shifted vibrational levels. Clear signatures always emerge at the appropriate revival times. We can conclude that PT excitation with appropriate $b$ and $c$ generates coherence patterns comparable with those obtained after ps evolution following FL excitation.

5.2. Perturbative treatment of PT excitation

Next, we want to confirm the assumptions about the analogies between the FL evolution and PT excitation on the basis of perturbation theory. We will derive formulae clarifying the effect of the pulse parameters $b$ and $c$ in close analogy to the FL pulse-induced WP evolution. Following time-dependent perturbation theory (TDPT) [62], we set up the total Hamiltonian (cf equation (1))

$$H = H_0 + \lambda H_1(t), \quad (16)$$

expand the wave function in a power series of the ordering parameter $\lambda$,

$$\Psi(t) = \Psi^{(0)}(t) + \lambda \Psi^{(1)}(t) + \cdots = \sum_n \lambda^n \Psi^{(n)}(t), \quad (17)$$

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and insert it into the TDSE (equation (1)). Under the assumption that the initial wave function at time $t_0$ is $\Psi(t_0) = \Psi^{(0)}(t_0)$, a recursion relation for the $n$th order state is obtained:

$$\Psi^{(n)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} e^{-(i/\hbar)H_0(t-t')} H_1(t') \Psi^{(n-1)}(t') dt'$$  \hspace{1cm} (18)

with the unperturbed wave function

$$\Psi^{(0)}(t) = e^{-(i/\hbar)H_0(t-t_0)} \Psi^{(0)}(t_0).$$  \hspace{1cm} (19)

To obtain an analytic expression, still covering the essentials of the mechanism induced, we consider a train of three $\delta$-function pulses of equal amplitude resonant to the vibrational level with maximum FC overlap and center frequency $\omega_n = (\omega_{\text{res}} - \omega_0)$, where $\omega_0$ and $\omega_{\text{res}}$ are the eigenfrequencies of the vibrational ground state of $V_g$ and the resonant vibrational level in $V_e$:

$$\epsilon(t) = \sum_{n=1}^{3} \delta(t - t_n) e^{-i\omega_n t} e^{i\phi_n}. $$  \hspace{1cm} (20)

Now the integrals in equation (18) can easily be evaluated. Introducing the energetic shift $\tilde{\omega}_n = \omega_n - \omega_{\text{res}}$ and under the assumption that in the low-excitation regime the backtransfer to vibrationally excited states of $\Psi_g$ is insignificant (an assumption that we proved in the course of the investigations), we can evaluate expressions for the first (equation (21))- and third (equation (23))-order wave functions, which describe the generated WP on the excited state $e$:

$$\Psi^{(1)}(t) = \frac{1}{i} \left( \sum_{t_n \in \{t_1, t_2, t_3\}} e^{i(\sum_n \tilde{\omega}_n)(t_n - t_2)} e^{-i\phi_n} \Psi_2^{(1)}(t) \right),$$  \hspace{1cm} (21)

where

$$\Psi_2^{(1)}(t) = e^{-i(\sum_n \omega_{\text{e,n}})(t-t_2)} e^{-i\omega_e t_2} e^{-i\phi_2} \mu e^{-i\omega_0 t_2} \Psi_g^{(0)}.$$  \hspace{1cm} (22)

is the first-order one-sided Feynman path induced by the central subpulse, $\omega_{\text{e,n}}$ are the energies of the vibrational levels of the electronic excited state $\Psi_e$ and $\omega_0$ is the ground-state energy, and

$$\Psi^{(3)}(t) = \left( \frac{1}{i} \right)^3 \left( \sum_{(t_{n1}, t_{n2}, t_{n3}) \in T^3} e^{i(\sum_n \tilde{\omega}_n)(t_n - t_2)} e^{-i(\sum_n \tilde{\omega}_n + 2\omega_0)(t_n - t_2)}
\times e^{i(\sum_{n \neq e} \phi_n)(t_n - t_2)} e^{-i(\phi_e + \phi_0 + \phi_3)} \Psi_2^{(3)}(t) \right),$$  \hspace{1cm} (23)

where

$$\Psi_2^{(3)}(t) = e^{-i(\sum_n \omega_{\text{e,n}})(t-t_2)} e^{-i\omega_e t_2} e^{-i\phi_2} \mu e^{-i(\omega_0)(t_2-t_2)} e^{-i\omega_e t_2} e^{-i\phi_2} \mu e^{-i(\sum_n \omega_{\text{e,n}})(t_2-t_2)}
\times e^{-i\omega_0 t_2} e^{-i\phi_2} \mu e^{-i\omega_0 t_2} \Psi_g^{(0)}$$  \hspace{1cm} (24)

is the third-order one-sided Feynman path induced by the central subpulse. We defined $T$ as the set of times appearing in the PT (equation (20)). In equations (21) and (23), each term in the sums describes the phase shift of a single Feynman path with respect to the one with exclusive
contributions of the central subpulse. The effect of the two parameters \( b \) and \( c \) can now be analyzed with these expressions.

The effect of \( b \) on the induced WPs can be evaluated already from the first-order wave function (equation (21)). Replacing the time difference \((t_n - t_2)\) between the pulses by \( b = \left(\frac{\alpha}{\beta} T_{cl}\right)\) and substituting equations (11), (12) and (13), we obtain

\[
\psi^{(1)}(t) = \frac{1}{i} \left( \sum_{t_1 \in \{t_1, t_2, t_3\}} \exp \left[ i \left( \sum_n \left( \frac{2\pi}{T_{cl}} (n - \tilde{n}) + \frac{1}{2} \left( \frac{2\pi}{T_{rev}} \right)^2 (n - \tilde{n})^2 \left( \frac{\beta}{\alpha} T_{cl} \right) \right) \right) \right] e^{-i\Phi} \psi^{(1)}_2(t).
\]

Equation (25) shows the same phase dependencies as derived for the evolution of the FL excited state in equation (14), verifying the analogies between FL and PT excitations. The important difference is the timescale for the revival pattern. In the case of FL pulses, the revivals happen on the ps timescale, while by PT excitation the same pattern can be obtained at the significantly shorter timescale of \( T_{cl} \) depending on the setting of \( b \) and \( c \).

The effect of the phase parameter \( c \) on the structure and dynamics of the WPs is much more complex and only present from the third order of TDPT. Evaluating equation (23) for different \( c \) values it becomes clear that the phase effect is not observed until summing up the single components, and therefore it is not possible to derive a simple formula to extract the effect of \( c \).

6. Conclusion and perspectives

In the present work, we analyzed the mechanism of PT excitation between molecular electronic states taking into account explicitly also the vibrational levels. Quantum dynamical simulations reveal effects like enhancement and annihilation of spectral amplitudes in the Fourier transform of the time-dependent autocorrelation function, similar to experimentally reported results. In a first step, we extracted phenomenological dependencies on the two multipulse parameters \( b \) and \( c \), defining the interpulse distance and the phase relation between single subpulses, respectively. The induced WP dynamics and the related frequency spectra could be best interpreted in Wigner representation. We could explain the symmetries formed and dissolved in the phase space structures and directly relate them to the signatures of selective enhancement or annihilation of individual peak amplitudes in the derived spectrum. By comparison to the dynamics following FL pulse excitation, we extracted analogies in the phase space pattern as well as in the deduced spectral signatures, which were helpful for the interpretation of the PT excitation mechanism and its final outcome. The origin of the phase space symmetries could be explained as well as how they transformed to specific spectral signatures. As an important difference, the timescales needed to generate certain WP patterns in the phase space, and thereby the corresponding spectrum, emerged. Individual WP patterns in Wigner space could be realized on a much shorter timescale by PT excitation compared with FL pulse excitation. In a final step, merging the results of the PT and the FL pulse-induced dynamics, we derived an analytic expression based on a perturbative description not only verifying the analogies between the two cases, but also allowing one to understand and even predict the outcome of PT excitation.

Our investigations lead to the conclusion that enhancement or annihilation of the spectral amplitudes following PT excitation has to be assigned to an interference effect, resulting from the phase shift of the coherences contributing to the spectra. Identical interference effects could be identified in a time- and frequency-resolved spectrum during the evolution of the FL

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pulse-excited WPs, however on the much longer timescale of $T_{rev}$. This interference effect is a pure coherent quantum mechanical phenomenon, based on the revival characteristics of the system under investigation. The expansion to higher dimensional systems should be straightforward and is the topic of ongoing work. From our results, we expect PT to have promising capabilities in the field of nonlinear spectroscopy. As possible applications for PT excitation in spectroscopic experiments, we predict a spectral resolution in the range of $T_{cl}$, which due to restrictions of Fourier transformation would only be reached on the much larger timescale of $T_{rev}$ for single FL pulse excitation. This feature may become especially interesting for the spectroscopy of short-living states, where the lifetime is restricted either due to dissipative effects or due to coherent loss channels, like for example conical intersections. The second promising point expected is the high sensitivity of phase $c$ at various values of $b$. With the right setting, a symmetric phase space state could be created, leading to selective amplitude damping in the frequency spectrum. Extrapolating this scenario to higher dimensional systems, the appropriate choice of $b$ and $c$ might allow for selective frequency damping, even in the case of close-lying frequencies, and could be most in tracking the dynamics of superimposed modes. Furthermore, PT should be extremely useful for nonlinear spectroscopy. The demonstrated selective control of coherences could be used in 2D spectroscopy, where the selective enhancement of single contributions to the spectra is a front topic of research.

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