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LETTERS

New Strategy for Optimal Control of Femtosecond Pump−Dump Processes

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We propose a new strategy for optimal control with tailored pump−dump pulses which drive a system of moderate complexity via electronically excited states to a desired objective in the ground state with a maximal yield. It is based on the concept of the intermediate target in the excited state which selects the appropriate Franck−Condon window at a given time delay between the two pulses mandatory for reaching optimally the objective. The existence of the intermediate target ensures the connective pathway between the initial state and the objective in the ground state, necessary for the controllability of multidimensional systems involving two electronic states. We show the scope of this concept by optimizing and analyzing the pump and dump pulses for driving the isomerization process in the Na_3F_2 cluster to the second isomer by suppressing radiationless transition through the conical intersection between the first excited and the ground state. This has been realized by employing our ab initio Wigner distribution approach.

I. Introduction

The optical control of chemical reactivity using tailored laser pulses interacting with molecules has been substantially advanced over the past years because of intense joint theoretical and experimental efforts (cf. refs 1 and 2 and references therein). Optimal control theory[3−8] and methods treating quantum interference phenomena[9,10] were used to compute the light fields which are able to drive a material system to a desired goal or objective. Simultaneously, the experimental development of techniques for ultrafast pulse-shaping made it possible to generate tailored light fields[11−16] which are able to suppress one pathway and to favour the other one.

It remains still to be answered whether optimal control involving more than one electronic state can be achieved for the systems with increasing complexity. In contrast to simple one-dimensional systems, here, at least two problems arise which have to be solved: The first one concerns the existence of the connective pathway between the initial state and the objective when the latter is reached via a different electronic state with distinct features, and the second is, even if this is ensured, how the optimal path can be found. To address this issue, we present in this contribution a combination of molecular dynamics, electronic structure calculation, and the development of a new optimal control strategy applicable to systems of moderate complexity. We consider the pump−dump control for two phase unlocked ultrafast fields in the weak response regime. A density matrix formulation is used based on our ab initio Wigner distribution approach.[17−19] This method combines the Wigner−Moyal representation of the vibronic density matrix with ab initio molecular dynamics (MD) in the excited and ground electronic states without precalculation of both energy surfaces and is therefore suitable for systems with a considerable number of degrees of freedom. The analysis of the classical trajectories obtained from the ab initio MD "on the fly" allows us to introduce the new strategy for optimal control through the concept of an intermediate target in the excited state which is

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valid for pulses on the very short fs time scale. The intermediate target is defined as a localized ensemble corresponding to the maximum overlap between the forward propagated phase space density on the electronic excited state (starting from the initial state) and the backward propagated phase space density from the objective, at the optimal time delay between the two pulses. The role of our intermediate target is to guarantee the connective pathway between the initial state and the objective and to use the excited-state ensemble for selecting the appropriate Franck–Condon window and the optimal time delay by sampling the portions of the both molecular energy surfaces involved. In fact, the latter is related to the inversion problem. The advantage of our optimal control strategy is also an easy access to underlying ultrashort processes reflected in the shape of the pulses because of the available analysis of the molecular dynamics. We illustrate the new optimal control strategy by optimizing pump and dump pulses for driving the isomerization process in the nonstoichiometric Na_3F_2 cluster, avoiding conical intersection between the ground and excited state,[19] and maximizing the yield in the second isomer.

II. Optimal Control Strategy

Starting from an initial thermal ensemble in the lowest energy isomer, our aim is to occupy maximally the second isomer, the objective, at a given time t_f by using a phase-unlocked pump–dump control strategy involving dynamics on the first excited state (pumping) and the ground state (dumping). Therefore, the temporal shape of both pulses and implicitly the time delay between them have to be optimized. This is, in general and also for the Na_3F_2 example, an optimization problem of a multidimensional system. For these systems, in the case of the isomerization process it is important to notice that the connective pathway between the initial state and the objective is guaranteed if the propagation on the first excited state can be controlled by the shaped pump pulse in such a way that the geometries related to the transition state between the two isomers in the electronic ground state can be reached. Then, the controlled shaping of the dump pulse induces the population transfer to the ground state and the localization of the population in the second isomer at t_f.

In the optimal phase-unlocked pump–dump control, the pump and dump pulses of the form $\epsilon_{P(D)}(t) = E_{P(D)}(t)\exp(-i\omega_{eg}t) + E^*_{P(D)}(t)\exp(i\omega_{eg}t)$ are considered, where $E_{P(D)}$ is a slowly varying envelope of the pump (dump) field, respectively, and ω_{eg} is the difference between the energies of the minima of the excited and the ground states. Variation with respect to the pulse envelopes $E_{P(D)}$ has to be performed in order to maximize the yield at the time t_f. In the case of the isomerization process, the objective in the ground state can be described in the Wigner representation by an operator $\hat{A} = A(\Gamma)|g\rangle\langle g|$ where $A(\Gamma)$ is the Wigner transform of the objective in the multidimensional phase space $\Gamma = \{q_i, p_i\}$ of coordinates and momenta, and $|g\rangle\langle g|$ is the ground state projection operator. Because we focus in our optimization problem to the maximal occupation of the second isomer, only the spatial localization of the phase space density is of relevance, and we assume an arbitrary distribution of the momenta. Thus, we write

$$A(p, q) = \prod_{i=1}^{N} \frac{1}{\sqrt{2\pi}\Delta q_i} e^{-(q_i-\bar{q}_i)^2/2(\Delta q_i)^2}\, \Theta\left(E_{\min} - \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m_i}\right) \quad (1)$$

where $\bar{q}_i$ denotes the Cartesian coordinates of the second isomer and Δq_i are the deviations. The Theta function ensures that the kinetic energy is kept below the lowest isomerization barrier $E_{\min}$.

Equations for the pulse envelopes to be optimized are obtained by considering the functional

$$J(t_f) = A(t_f) - \lambda_P \int_0^{t_f} |E_P(t)|^2\, dt - \lambda_D \int_0^{t_f} |E_D(t)|^2\, dt \quad (2)$$

The last two terms are due to the general constraint of the finite total energy of the pump and the dump pulses, respectively, and $A(t_f)$ is the yield at the time t_f which can be calculated in weak field second-order perturbation theory[8,20,21] and in the framework of the Wigner representation according to

$$A(t_f) = \int\!\!\int d^2\Gamma_0 \int_0^{t_f} d\tau \int_0^{\tau} d\tau' \int_0^{\tau'} d\tau'' \int_0^{\tau''} d\tau'''\, A(\Gamma_g(t_f - \tau;$$
$$\Gamma_e(\tau' - \tau''; \Gamma_0)))e^{i(\omega_{eg} - U_{ge}(\Gamma_e(\tau'-\tau'';\Gamma_0)))(\tau-\tau')} e^{i(\omega_{eg} - U_{ge}(\Gamma_0))(\tau''-\tau''')} \times$$
$$\rho_{gg}(\Gamma_0) E_P(\tau''') E_P^*(\tau'') E_D(\tau') E_D^*(\tau) \quad (3)$$

This expression involves the propagated excited and ground-state ensemble Γ_e and Γ_g induced by the pump and the dump pulses, respectively. U_{eg} in eq 3 is the time-dependent energy gap between the states, and $\rho_{gg}(\Gamma_0)$ denotes the initial distribution of the phase space Γ_0 in the Wigner representation. Optimal field envelopes are obtained by calculating the extrema of the control functional eq 2 from a variational procedure. This leads to the following pair of coupled integral equations for the field envelopes of the Fredholm type:

$$\int_0^{t_f} d\tau'\, M_P(\tau, \tau'; E_D)\, E_P(\tau') = \lambda_P E_P(\tau) \quad (4)$$

$$\int_0^{t_f} d\tau'\, M_D(\tau, \tau'; E_P)\, E_D(\tau') = \lambda_D E_D(\tau) \quad (5)$$

where the integral kernels usually denoted as material response functions are given by

$$M_P(\tau, \tau'; E_D) = \int\!\!\int d^2\Gamma_0 \int_0^{t_f} d\tau'' \int_0^{\tau''} d\tau'''\, A(\Gamma_g(t_f - \tau'';$$
$$\Gamma_e(\tau''' - \tau; \Gamma_0)))e^{i(\omega_{eg} - U_{eg}(\Gamma_e(\tau'''-\tau;\Gamma_0)))(\tau''-\tau''')} e^{i(\omega_{eg} - U_{eg}(\Gamma_0))(\tau-\tau')} \times$$
$$\rho_{gg}(\Gamma_0) E_D(\tau''') E_D^*(\tau'') \qquad \tau \geq \tau' \quad (6)$$

$$M_D(\tau, \tau'; E_P) = \int\!\!\int d^2\Gamma_0 \int_0^{\tau'} d\tau'' \int_0^{\tau''} d\tau'''\, A(\Gamma_g(t_f - \tau;$$
$$\Gamma_e(\tau' - \tau''; \Gamma_0)))e^{i(\omega_{eg} - U_{eg}(\Gamma_e(\tau'-\tau'';\Gamma_0)))(\tau-\tau')} e^{i(\omega_{eg} - U_{eg}(\Gamma_0))(\tau''-\tau''')} \times$$
$$\rho_{gg}(\Gamma_0) E_P(\tau''') E_P^*(\tau'') \qquad \tau \geq \tau' \quad (7)$$

These coupled nonlinear integral equations can be solved iteratively giving a solution for optimal pump and dump fields. However, this is computationally a very demanding task even for systems of moderate complexity because coupled classical trajectory simulations on the ground and excited states have to be performed. In fact, the calculation of the objective function A in eqs 6 and 7 requires the propagation of the ensemble onto the ground state Γ_g starting at different initial conditions which are obtained from the propagated ensemble Γ_e of the excited state at every time step.

However, we will show in the following that by restricting the optimization problem to field envelopes in the fs regime a new strategy can be proposed which reduces the problem to solving single Fredholm-type integral equations for the optimal pump and dump fields at acceptable computational demand. Our strategy involves the following steps:

(i) It is justified in the ultrashort time approximation and in the zeroth order of an iterative procedure to calculate the kernel functions M_P and M_D with strongly localized pulse envelopes $E_P \propto \delta(t)$ and $E_D \propto \delta(t - t_d)$ where t_d is the time delay between the pulses to be determined. This yields for the zeroth order material response functions eqs 6 and 7:

$$M_P^{(0)}(\tau, \tau') = \int\int d^2\Gamma_0\, A(\Gamma_g(t_f - t_d; \Gamma_e(t_d - \tau; \Gamma_0))) \times e^{i(\omega_{eg} - U_{eg}(\Gamma_0))(\tau - \tau')}\rho_{gg}(\Gamma_0) \qquad \tau \geq \tau' \quad (8)$$

$$M_D^{(0)}(\tau, \tau') = \int\int d^2\Gamma_0\, A(\Gamma_g(t_f - \tau; \Gamma_e(\tau'; \Gamma_0))) \times e^{i(\omega_{eg} - U_{eg}(\Gamma_e(\tau'; \Gamma_0)))(\tau - \tau')}\rho_{gg}(\Gamma_0) \qquad \tau \geq \tau' \quad (9)$$

Obviously, in this approximation, the equations for the pump and the dump fields are decoupled. According to eq 8, the pump pulse optimization involves the propagation on the excited state $\Gamma_e(t_d - \tau)$ from $\tau = 0$ until t_d starting from the initial ensemble Γ_0, whereas for the dump pulse optimization, eq 9, the dynamics on the ground state $\Gamma_g(t_f - \tau; \Gamma_e(t_d))$ for $\tau' = t_d$ until t_f has to be performed with initial conditions given by the ensemble of the excited state $\Gamma_e(t_d)$ at t_d. We call the ensemble $\Gamma_e(t_d)$ at t_d the intermediate target which can be determined from the maximal overlap between a forward propagated ensemble from the first isomer on the excited state and a backward propagated ensemble from the second isomer on the ground state.

(ii) The optimized pump pulse in first order of the iterative procedure can be calculated from eqs 4 and 8 which localizes the phase space density at the intermediate target.

(iii) Optimization of the dump pulse by solving eqs 5 and 9 projects the intermediate target to the ground state and localizes the phase space density into the objective at the specified final time t_f.

It should be pointed out that the mentioned problem of the connective pathway between the initial state and the objective is related to the existence of the intermediate target at a time t_d. The condition for this is that the function $A(\Gamma_g(t_f - t_d; \Gamma_e(t_d)))$ has nonvanishing contributions as it follows from eqs 8 or 9 which can be found from classical trajectory simulations.

The described procedure can be in principle continued iteratively leading to fully optimized pump and dump pulses. However, in many practical cases, as we will show in the next section, it can be expected that the zeroth and first order iteration leads to sufficient accuracy. With our strategy involving the concept of the intermediate target, we have succeeded in reaching the objective with the maximum yield by optimizing the pulses independently, which is computationally acceptable even for the systems of moderate complexity. At the same time, the analysis of the ensemble of trajectories corresponding to dynamics in the excited and in the ground states allows easy interpretation of the shaped pulses and the underlying ultrashort processes.

III. Optimal Control of the Isomerization in Na_3F_2

In this section, we apply the concept of the intermediate target to the pump−dump-induced isomerization of the Na_3F_2 cluster. The aim of the investigation is to gain an understanding of the mechanisms behind the pump−dump control processes including the estimate of the efficiency of the controlled isomerization. The choice of the Na_3F_2 cluster with nine degrees of freedom is particularly suitable because two isomers with different structures and the transition state separating them with a relatively low barrier of 0.12 eV are present. The lowest energy isomer I (cf. lower part of Figure 1) with C_s symmetry is characterized by the Na atom bound to the ionic Na_2F_2 subunit, and in the second isomer II with C_{2v} symmetry, a metallic Na_3 subunit is bicapped by the F atoms.[22] Because of strong ionic bonds, the first excited state arises primarily by the excitation of the single excess electron. The first excited state exhibits a shallow local minimum (not shown) related to the transition state of the ground state and the global minimum with a linear geometry corresponding to a conical intersection between the ground and the first excited state (cf. Figure 1) which has been fully characterized in our previous work.[19] The isomerization through the conical intersection is characterized by a large excess of energy (≈0.65 eV), and therefore, a population of only the single isomer II is excluded by this nonradiative transition. Thus, another pathway due to optimal control is preferable for reaching the objective with a maximal yield. For this purpose according to the optimal control strategy described in section II, we first generate an initial ensemble of the C_s isomer, then determine the intermediate target involving excited state and ground state dynamics, and finally optimize the pump and the dump pulses.

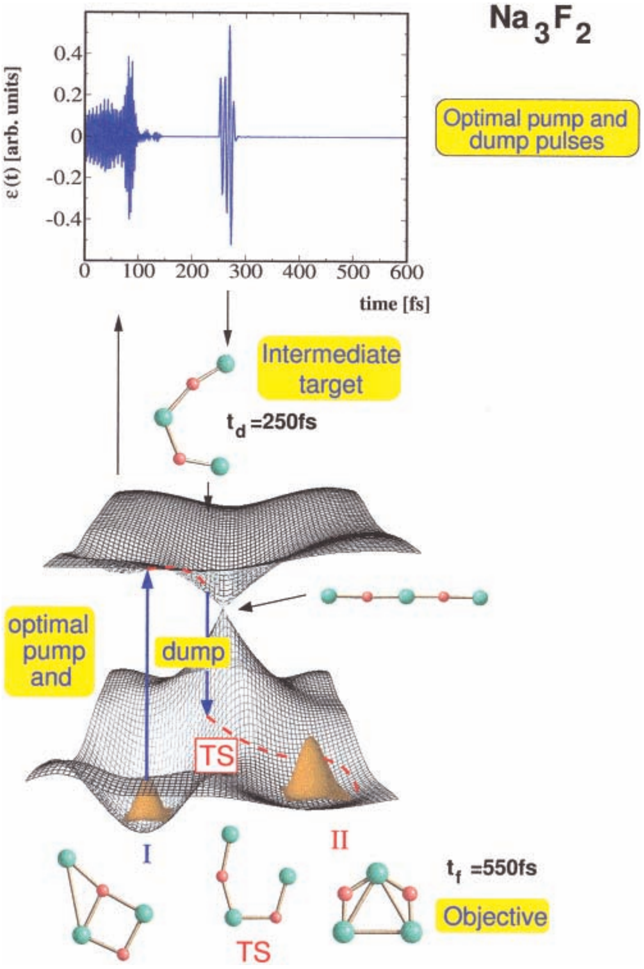

Figure 1. Scheme for the pump−dump optimal control in the Na_3F_2 cluster with geometries of the two ground-state isomers and the transition state separating them, the conical intersection, and the intermediate target. The optimal electric fields corresponding to the pump and dump pulses are shown in the upper part. The mean energy of the pump pulse is 1.20 eV, and the mean energy of the dump pulse is 0.6 eV.

Our ab initio Wigner distribution approach involving ab initio MD "on the fly" for the excited and the ground states, as described in refs 18 and 19, has been used throughout the paper. This method yields an accurate description of ultrashort processes as illustrated on the example of Na_2F by comparing the measured pump−probe signals with the simulated ones. The excellent agreement between the theoretical and experimental pump−probe signals allowed for the identification of periodic geometrical rearrangements between the linear and bend structures in the first excited state of Na_2F because of the breaking of the Na−Na bond.[23]

In this contribution, we assumed for the initial ensemble a 50 K temperature canonical distribution in the ground state of the C_s Na_3F_2 isomer I in Wigner representation (cf. eq 27 of ref 18 with ω_i being the nine normal modes of Na_3F_2) given by a set of 800 coordinates and momenta. The ensemble was propagated classically for 300 fs on the first excited state which corresponds to the vertical excitation energy of 1.33 eV (pump step). To define the intermediate target and the optimal time delay t_d (cf. section II), the ensemble was dumped back to the ground state every 25 fs and subsequently propagated for 1 ps. It was found that the objective can be reached by the ensemble at $t_d = 250$ fs where residence times of at least 500 fs within the C_{2v} basin were observed. The ensemble averaged geometry after $t_d = 250$ fs defining the coordinates $\bar{q}_i$ of the intermediate target is shown in Figure 1. It should be noted that also for time delays larger than 250 fs the objective could be reached. However, the residence times and the occupation is much smaller because of the larger excess of energy gained by the propagation on the excited state. The analysis of the ensemble averaged momenta after $t_d = 250$ fs defining the momenta $\bar{p}_i$ of the intermediate target has shown that it is directed in the way which leads to the second isomer II. The averaged kinetic energy in the intermediate target corresponds to about 75% of the isomerization barrier in the ground state. This guarantees that the ensemble remains localized in the basin corresponding to the isomer II after the dump.

Next we consider the optimization of the pump pulse leading to a localization of the phase space density in vicinity of the intermediate target. Thus, for the intermediate target operator in Wigner representation (eq 8), we assume a minimum uncertainty wave packet of the form

$$A(p_i, q_i) = \prod_{i=1}^{3N=15} \frac{1}{2\pi\Delta p_i \Delta q_i} e^{-(q_i-\bar{q}_i)^2/2(\Delta q_i)^2} e^{-(p_i-\bar{p}_i)^2/2(\Delta p_i)^2} \qquad (10)$$

where the uncertainties in the coordinates Δq_i were defined such that they correspond to the spreading of the initial ensemble which is about 0.053 Å, and the uncertainties in the momenta are given by $\Delta p_i = 1/\Delta q_i$. The material response function $M(\tau, \tau')$ for the pump pulse (eq 8) was calculated on a time grid with a spacing of 1 fs, then symmetrized, and finally, according to eq 4, diagonalized using the standard Jacobi procedure. The largest eigenvalue which corresponds to the globally optimal pump pulse was obtained to be 0.82 which corresponds to a 82% efficiency of localizing the ensemble in the intermediate target. The optimized pump pulse obtained from eq 4 has a complex temporal shape where the envelope consists of two portions corresponding to ≈70 and ≈10 fs (cf. first part of the upper panel of Figure 1). Physical insight can be gained by considering the Fourier transform and the Wigner transform of the pump pulse (cf. Figure 2 parts a and b). Obviously, comparing the Fourier transform with the initial Franck−Condon profile of the C_s isomer (Figure 2a), the excitation of the low lying Franck−Condon transition around 1.2 eV of the initial ensemble is mainly responsible for reaching the intermediate target. This spectral region corresponds to lower lying vibrational modes which opens the C_s structure by breaking of the Na−Na bond and one Na−F bond. The Wigner transform (Figure 2b) shows that this energetically sharp transition corresponds to the first temporal portion (≈70 fs) of the pulse, whereas the very short second portion after 80−90 fs with the duration of ≈10 fs is energetically much wider. The latter region is related to the lower lying and higher lying tails of the Fourier transform (Figure 2a) which are symmetric with respect to the 1.2 eV transition reflecting the fact of equally distributed velocities in the initial ensemble.

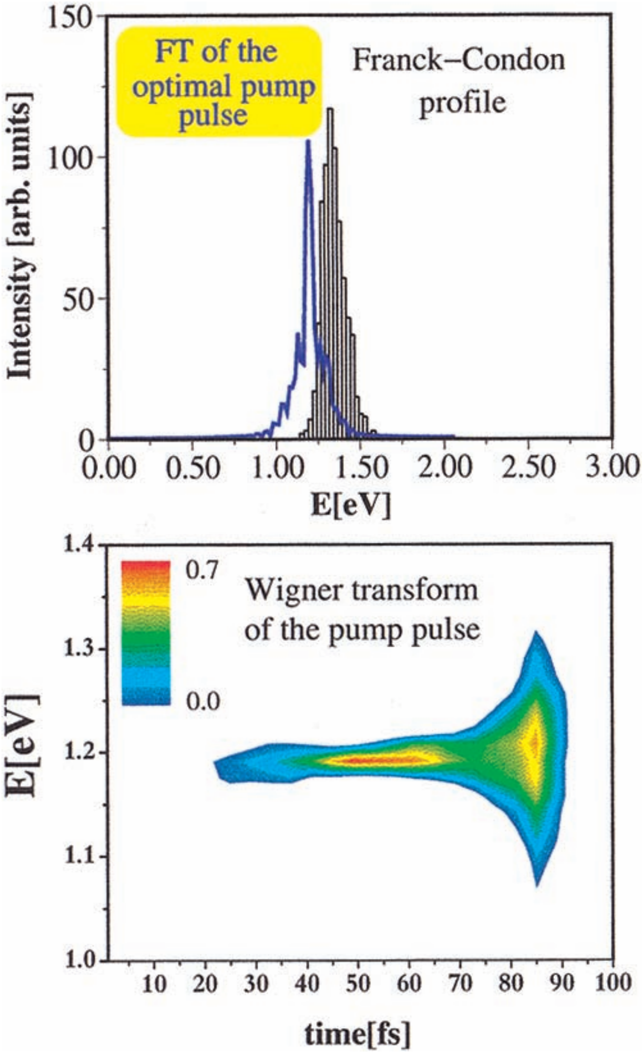

Figure 2. Fourier transform of the optimal pump pulse and the Franck−Condon profile for the first excited state corresponding to the excitation energy $T_e = 1.33$ eV (upper panel (a)) and Wigner transform of the optimal pump pulse (lower panel (b)).

For the dump pulse optimization leading to spatial localization of the phase space density in the objective, the intermediate target operator (eq 10) was propagated on the ground state and the dump pulse was determined from the solution of eqs 5 and 9. The largest eigenvalue obtained was 0.78 corresponding to 78% efficiency of the localization in the second isomer. The obtained dump pulse with a duration of only ≈20 fs (cf. second part of the upper panel of Figure 1) gives the evidence that the time window around t_d for the depopulation of the excited state induced by the dump pulse is very short in accordance with the fact that the system rapidly gains a large amount of excess energy on the excited state. The Fourier transform of the dump pulse (not shown) is centered around 0.6 eV corresponding to the Franck−Condon transition energy at t_d.

Figure 3 shows snapshots of the ground-state ensemble propagated onto the ground state after the dump process. It can be seen that the ground-state phase space density is catched

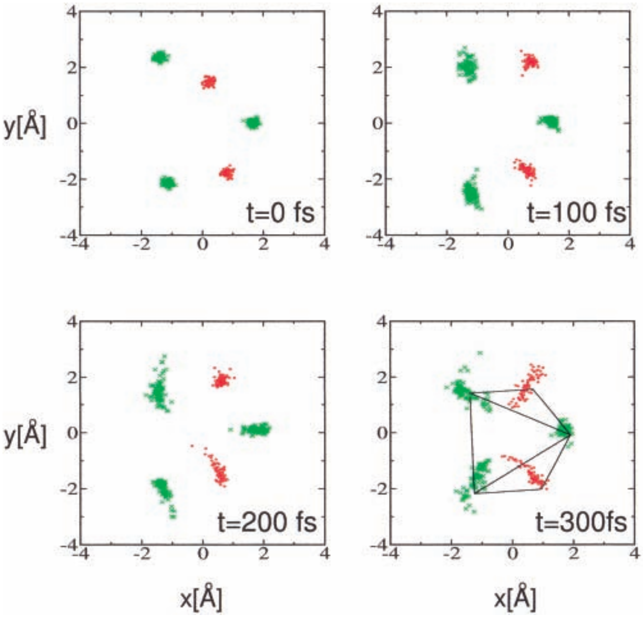

Figure 3. Snapshots of the dynamics obtained by propagating the ensemble corresponding to the intermediate target after the optimized pump−dump at 250 fs on the ground state showing the localization of the phase space density in the basin corresponding to the isomer II.

within the C_{2v} basis after about $t_d + 200$ fs $= 450$ fs. The analysis of the ensemble dynamics has shown that the residence time is about 500 fs.

IV. Summary

We developed a new strategy for optimal pump−dump control in multidimensional systems by introducing the concept of the intermediate target in the excited state. Its role is to select the appropriate Franck−Condon window at a given time delay between the two pulses by sampling parts of the energy surfaces and ensuring the connective pathway between the initial state and the objective as well as the optimal yield. This is a necessary condition for carrying out the decoupled iterative optimization procedure for the pump and dump pulses related by the optimized dump time, which allows for a decrease in the computational demand and permits the applications to larger systems. We showed on the example of Na_3F_2 that optimized pulses drive the isomerization process in the desired objective, the second isomer. The analysis of the MD and of the tailored pulses allows us to identify a mechanism based on the selection of appropriate vibrational modes responsible for optimal control. This opens the possibility for the optimal control of complex systems under the condition that the intermediate target can be found. The gained knowledge about pulse shapes can be used to introduce a guidance toward the understanding of experimentally shaped pulses. At the same time, the controlled population of such a bimodal system might provide a basis for constructing the molecular “flip−flop” switch which can be used for information storage.[24]

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