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The ability to prepare a specific superposition of electronic excited states leading to a transitory symmetry breaking of the electronic density in complex systems remains a challenging concern. We investigate how an initial coherence can be controlled by laser fields. The selected molecular system is a symmetric dimer of phenylene ethynylene presenting different interesting properties: two bright nearly degenerate excited states coupled through a conical intersection are addressable by orthogonal transition dipole moments and are well separated from neighboring states. Creating a superposed state with equal weights corresponds to a right or left electronic localization as in the double-well system followed by a transitory oscillation between the two wells. To ensure a spectral bandwidth typically smaller than 0.25 eV, the pulse duration is in the tens of femtoseconds range so that nuclear motion cannot be neglected. Optimal control theory (OCT) is applied with guess fields that effectively create the target coherence in the absence of dephasing due to the vibrational baths. We analyze the field reshaping proposed by the control and we further fit sequence of pulses on the optimal field. The overall result is efficient and robust disymmetry control over reasonable time scales of few tens of femtoseconds, exceeding the pulse duration. The monotonically convergent algorithm is combined with the hierarchical equations of motion (HEOM) able to treat strongly coupled non-Markovian dynamics. We also check the implementation of the combined OCT-HEOM approach in the tensor-train (TT) representation with propagation using the time dependent variational method.

I. INTRODUCTION

Controlling electron dynamics and quantum coherence to trigger particular nuclear displacements is the basic concern of the emerging field of atto-physics and femto-chemistry [1–7]. The preparation by laser fields of specific superpositions of excited eigenstates generates an electron density reorganization or symmetry breaking [8, 9] and the correlated directional properties on the nuclear motion.

The timescale of the light pulse fixes the spectral bandwidth and this could be prohibitive when the target is a narrow band of some particular bright excited states. To avoid interference with additional bright states, the pulse duration should not be less than few tens of femtoseconds. It is then similar to some vibrational periods and electronic decoherence will occur during the interaction with the laser field. The variation of the off-diagonal elements of the reduced density matrix is due to relaxation induced here by the non-adiabatic transitions and to dephasing caused by the tuning of the energies. Developing strategies to improve the preparation of superposed electronic states and to preserve coherence at least during the pulse remains a challenging objective in complex molecular systems [10–16]. Our goal concerns the timely issue of optimizing control procedures for quantum systems strongly coupled to structured environments and leading to non-Markovian reduced dynamics. This requires implementing an optimization procedure of the parametric space among numerous available methods [17–24] with an efficient treatment of non-Markovian open systems [16, 25–27]. There are two main ways to account for the non-Markovianity reviewed for instance in reference [28]. The dimension of the active system may be increased by including a reasonable number of discrete modes while the residual bath is weakly coupled and Markovian [29–37]. The other scenario simulates the baths by continuous spectral densities leading to time-local coupled hierarchical equations of motion (HEOM) [38–41]. In this work, we combine HEOM with a monotonically convergent algorithm of optimal control theory (OCT) in presence of dissipation [42]. For non-Markovian dissipation, the backward propagation to solve the equation with the final target condition requires special attention [43]. This is established at the second order [44] and generalized for HEOM [27]. We compare the approach using a standard Cash–Karp Runge–Kutta adaptive algorithm [45] with a tensor train (TT) representations [37, 46–52] recently implemented in HEOM [53–56].

We consider a symmetric molecular system: a meta-substituted dimer of phenylene ethynylene (PPE) of C_{2v} symmetry, which is a building block of tree-like dendrimers [57–59]. The first excited manifold is composed of two quasi-degenerate bright states (the gap at the Franck-Condon geometry is 0.044 eV) of different symmetry only radiatively coupled to the ground state. The two states are coupled through a conical intersection

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[60], characterized in reference [61]. The model is calibrated from molecular *ab initio* data in the framework of the Linear Vibronic Coupling (LVC) model currently used to describe conical intersections [62]. The adiabatic excited states are delocalized over the whole nuclear skeleton. Our aim is to create a superposed excited state with a broken symmetry leading to a transitory localization on the left or right part of the molecule (see figure 1).

For the optimization, we first explore guess fields inspired from a simplified three-state V-type model without dissipation for which there is an analytical solution based on simultaneous $\pi/\sqrt{2}$ pulses with orthogonal polarization and equal duration [63]. In a second step, we use OCT with an optimization on a time grid to offer the maximum flexibility to the pulse shape. The interpretation of the resulting reshaped optimized field actually suggests a sequence of few pulses which can further be designed by shaping techniques. Still another way is to provide simple analytical forms for the individual pulses and fit their parameters with the optimized field.

The paper is organized as follows: in Section II, we present the *ab initio* data and particularly, the parameters of the LVC model of the conical intersection between the excited states. Section III describes the spectral densities of the tuning and coupling baths, paying particular attention to the correlation of the tuning baths. In Section IV, we explicit the strategies for the field driven dynamics. The results are given in Section V. All the equations for the OCT-HEOM approach are summarized in Appendix A and the TT representation is given in Appendix B. Appendix C provides a list of the abbreviations.

II. MODEL

The molecular system is a C_{2v} meta-substituted dimer of phenylene ethynylene (PPE). We focus on the first excited manifold with two bright excited states S_1 ($1B_2$) and S_2 ($2A_1$) coupled to the ground S_0 ($1A_1$) state only radiatively through corresponding transition dipoles. All calculations were performed with the Gaussian16 package (revision A03) [65] using DFT (ground state, S_0) and TD-DFT (excited states, S_1 and S_2) at the CAM-B3LYP/6-31+G* level of theory, the validity of which having been already assessed in previous works [61, 64]. The electronic-state symmetries, energies, and oscillator strengths at the S_0 minimum and S_2/S_1 Minimum Energy Conical Intersection (MECI) geometries are provided in the Supplemental Material. It also contains the geometries of the S_0 minimum and S_2/S_1 MECI.

The molecule is planar and positionned according to Mulliken's axis convention for C_{2v} symmetry (as shown in figure 1). More precisely, z (A_1) is the C_2 rotation axis, y (B_2) lies within the molecular plane, and x (B_1) is orthogonal to it. The vertical energies and the dipole transition moments at the ground equilibrium geometry

(minimum of S_0) are given in figure 1. The two excited states are coupled through a conical intersection that has been recently characterized [61]. This induces an ultrafast nonadiabatic funneling between these states. We consider the A_1 and B_2 in-plane motions by discarding soft out-of-plane torsions, which are expected to play a secondary role. The S_1 and S_2 states may cross in C_{2v} symmetry. The S_1 state exhibits two equivalent minima in C_S geometry connected by B_2 deformations. A scheme of the adiabatic potential energy surfaces is given in figure 1. This adiabatic representation may be described in terms of two interesting diabatic basis sets leading to the so-called delocalized or localized diabatic states respectively [66]. The delocalized states are adapted to the A_1 or B_2 symmetries. They coincide with the adiabatic states along symmetry conserving A_1 motions, which are the tuning modes making fluctuate the energy gap. They are coupled by a potential electronic coupling along B_2 modes, which are the coupling modes. In the LVC model, the two excited delocalized diabatic states are written in mass weighted coordinates by choosing the Franck-Condon geometry as a reference point and by neglecting any Duchinsky rotation of the normal modes. Accordingly, the N normal modes q_j are the same in each electronic state, only their equilibrium position $q_{j,0}^{(m)}$ depends on the electronic state m. The N normal modes are separated in tuning and coupling classes $N = N_t + N_c$ according to their symmetry, the corresponding modes being denoted $q_{j,t}$ or $q_{j,c}$ respectively. The Hamiltonian matrix in the delocalized diabatic basis set reads:

$$H_{mm}^{deloc} = \varepsilon_{FC}^{(m)} + 1/2 \sum_j^N \left(p_j^2 + \omega_j^2 q_{j,t/c}^2 \right) - \sum_j^{N_t} d_j^{(m)} q_{j,t} \tag{1}$$

$$H_{mm'}^{deloc} = \sum_j^{N_c} c_j^{(mm')} q_{j,c} \tag{2}$$

where $\varepsilon_{FC}^{(m)}$ is the energy at the Franck-Condon geometry. In the harmonic model, the gradients $d_j^{(m)} = \omega_j^2 q_{j,t,0}^{(m)}$ are related to the distance $q_{j,t,0}$ between the minimum position of the excited state and the reference point. A good agreement of the two values is a validation of the harmonic hypothesis. The gradients of the coupling are computed by a method detailed in reference [67]. The components of relevant shifts and gradients in terms of in-plane normal modes (A_1 and B_2) are listed in the Supplemental Material. They lead to the definition of collective coordinates ensuring the whole coupling to the electronic system

$$X_t^{(m)} = \sum_j^{N_t} d_j^{(m)} q_{j,t} / D_{0t}^{(m)} \tag{3}$$

and

$$X_c^{(mm')} = \sum_j^{N_c} c_j^{(mm')} q_{j,c} / D_{0c}^{(mm')} \tag{4}$$

with $D_{0t}^{(m)} = \sum_j^{N_t} d_j^{(m)2}$ and $D_{0c}^{(mm')} = \sum_j^{N_c} c_j^{(mm')2}$. In figure 1, we illustrate the main vibrational tuning
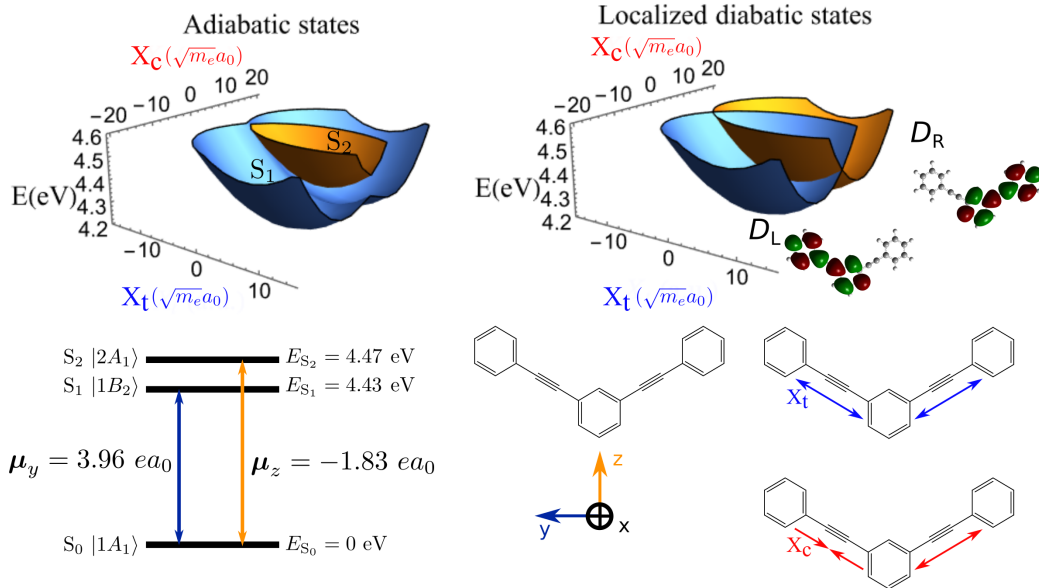
Figure 1. Upper panel: 3D-schematic view of the conical intersection between the adiabatic excited states S_1 and S_2 (left panel) and of the corresponding localized diabatic states D_L and D_R with their corresponding electronic LUMO orbitals [61, 64] (right panel). Lower panel: *ab initio* energies and transition dipole moments at the minimum geometry of the ground state S_0 (left part). The x, y and z-axes convention together with the main vibrational mode X_t of A_1 symmetry belonging to the tuning bath and the main antisymmetric coupling bath mode X_c of B_2 symmetry are illustrated in the right part.

and coupling modes contributing to the effective coordinates. They are the high-frequency stretching modes of the two triple bonds connecting the phenyl rings with the symmetric A_1 deformation for $X_t^{(m)}$ and the antisymmetric B_2 one for $X_c^{(mm')}$ respectively.

By transforming the two-by-two subspace of the excited delocalized diabatic basis set by a $\pi/4$ rotation matrix, the equilibrium positions of the diabatic localized states D_L and D_R correspond to those of the adiabatic lowest state, which displays a double well profile along a B_2 displacement. Each localized diabatic state corresponds to the localization of the excited electronic density on one or the other side of the dimer as illustrated in figure 1.

III. OPEN QUANTUM SYSTEM

According to the open quantum system approach, the full vibronic space is partitioned into an active subsystem explicitly treated quantum mechanically and its surrounding addressed as a bath. The choice of the partition is a key ingredient to get a computationally tractable master equation. Hierarchical equations of motion (HEOM) are one of the standard strategies to solve the system-bath dynamical equations in a numerically exact way provided that the bath is harmonic and linearly coupled to the system. Different partitions have been used in HEOM applications with a conical intersection by including in the active system the main tuning and coupling modes and the corresponding potential energy surfaces coupled to residual baths [68], or only the electronic subsystem at a reference geometry (here the equilibrum geometry of the ground electronic state) [63, 69, 70], the baths being all the nuclear tuning or coupling vibrational modes at thermal equilibrium at the reference point. We adopt the second strategy. The full Hamiltonian is then rewritten as:

$$H = H_S + H_{SB} + H_B \qquad (5)$$

where H_S is the diabatic delocalized symmetry adapted electronic Hamiltonian at the Franck-Condon geometry. At this reference point, the diabatic and adiabatic energies coincide and the coupling vanishes. The energies are given in figure 1. The transformation to the localized diabatic representation

$$H_S^{loc} = U^\dagger H_S U \qquad (6)$$

involves the matrix

$$U = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}. \qquad (7)$$

The system-bath coupling is $H_{SB} = \sum_b S_b B_b$ where $b = t, c$ designates the bath. S_b and B_b are operators of the electronic and of the complementary vibrational spaces respectively. The linear coupling is induced by the antisymmetric coupling modes, which are coupled

off-diagonally by the operator $S_c = |S_1\rangle\langle S_2| + |S_2\rangle\langle S_1|$. The tuning baths inducing fluctuation of the energy gaps are often considered as independent when they gather modes belonging to different molecular sites embedded in complex structures as in light harvesting complexes. The operator relating each tuning bath is then the projector on the corresponding electronic state $S_{t,m} = |m\rangle\langle m|$ and the total contribution to the coupling term is $S_{t,m_1}B_{b_1} + S_{t,m_2}B_{b_2}$. In the case of the conical intersection in a single molecular system, the modes are assumed to be the same in the excited electronic states. When some modes lead to different gradients in the different states, they are correlated and make appear cross terms in the correlation function of the bath modes. An approximate way of accounting for bath correlation is to work with a single bath coupled via a composite operator $S_t = |m\rangle\langle m| + w|m'\rangle\langle m'|$. Limit values $w = 1$ or $w = -1$ correspond to fully correlated or anticorrelated baths, i.e. each mode leads to the same gradient or the opposite gradient in the two electronic states [71]. We take a model with a constant correlation factor fixed by the principal A_1 mode leading the largest gradient and we use the operator $S_t = |S_1\rangle\langle S_1| + 0.893|S_2\rangle\langle S_2|$ as discussed below when we present the bath spectral densities. A more sophisticated method introducing a frequency dependent correction of the spectral density has been used recently [72].

The bath operators are collective modes having the dimension of an energy. For the correlated tuning baths involving the composite operator S_t, we use the tuning collective mode $B_t = \sum_j^{N_t} d_j^{(S_1)} q_{j,t} = D_{0t}^{(S_1)} X_t^{(S_1)}$ where $d_j^{(S_1)}$ are the S_1 gradients at the reference point. The coupling collective mode is $B_c = \sum_j^{N_c} c_j^{(S_1 S_2)} q_{j,c} = D_{0c}^{(S_1 S_2)} X_c$ where $c_j^{(S_1 S_2)}$ are the gradients of the interstate coupling.

The key tool is the spectral density

$$J_{t/c}(\omega) = \frac{\pi}{2}\sum_j f_j^2 \omega_j^{-1}\delta(\omega - \omega_j) \tag{8}$$

where f_j^2 is the strength of the coupling at each frequency and $f_j = d_j$ or $f_j = c_j$ for t/c respectively. It is linked to the so-called thermal spectral density $J_{t/c}^T(\omega) = J_{t/c}(\omega)\left(e^{\beta\omega} - 1\right)^{-1}$ with $\beta = 1/k_B T$. $J_{t/c}^T(\omega)$ is used in different approaches with discrete modes to account for the temperature. In the continuous approach, the master equation involves the Fourier transform $C_{t/c}(t) = \int_{-\infty}^{\infty} d\omega J_{t/c}^T(\omega)e^{-i\omega t}$ that is the two-time correlation function of the collective modes $C_{t/c}(t) = \langle B_{t/c}(t)B_{t/c}(0)\rangle_{eq}$ where $B_{t/c}(t)$ is the Heisenberg representation of the operator and $\langle\cdot\rangle_{eq}$ denotes the average over a Boltzmann distribution at temperature T. The delta distribution of the discrete spectral density is broadened by a Lorentzian smoothing function $\delta(\omega - \omega_j) \rightarrow \frac{1}{\pi}\frac{\Gamma}{(\omega - \omega_j)^2 + \Gamma^2}$ [73–75]. In this work, we used Γ with a wave number 160 cm^{-1}. The
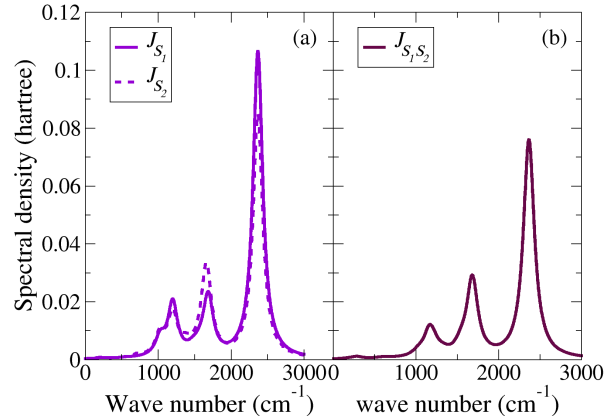

Figure 2. Discrete spectral densities (Eq.(8)) broadened by a Lorentzian function with a width of wave number 160 cm^{-1}. Panel(a): J_{S_1} and J_{S_2} of the tuning baths; panel(b): $J_{S_1 S_2}$ of the coupling bath.

tuning spectral densities of the two excited states denoted J_{S_1} and J_{S_2} are given in figure 2(a). Figure 2(b) displays the spectral density of the coupling bath $J_{S_1 S_2}$. The smooth spectral densities have been fitted by three two-pole Tannor-Meier Lorentzians [76].

$$\mathcal{J}_{t/c}(\omega) = \sum_i^{N_{l,t/c}} \frac{p_i\omega}{\left[(\omega + \Omega_i)^2 + \Gamma_i^2\right]\left[(\omega - \Omega_i)^2 + \Gamma_i^2\right]} \tag{9}$$

where $N_{l,t/c}$ is the number of two-pole Lorentzians in the tuning or coupling bath. The fitted functions and their parameters are given in the Supplemental Material. The main components are the high frequency modes corresponding to the symmetric (wave number 2367.4 cm^{-1}) and antisymmetric (wave number 2366.5 cm^{-1}) streches of the acethylenic bond (see Fig.1). The central peaks at wave number 1692.1 cm^{-1} for the tuning modes and wave number 1681.9 cm^{-1} for the coupling ones are associated to A_1 or B_2 in-plane deformations of the central benzene ring. The third peak corresponds to secondary contributions to the tuning (A_1 at 1199 c cm^{-1}) and to the coupling (B_2 at 1160 c cm^{-1}) modes. They describe in-phase and out-of-phase stretches of the bonds linking the acetylenic moieties to the benzenic ones, respectively, with induced in-plane triangular distortions of the rings.

We assume a positive correlation between the S_1 and S_2 tuning baths independent of the frequency and fixed by the high frequency modes with wave number 2367 cm^{-1}. This approximation seems reasonable and reduces the computational effort by introducing a single tuning bath and a composite system-bath operator.

The partition of the electronic system leads to highly non-Markovian dynamics. The non-Markovianity is related with the flow-back of information from the baths to the system. In the case of this electronic partition,

it results from the possible recurrence of a partial vibrational wave packet in the initial Franck-Condon region during the non-adiabatic dynamics. This leads to a signature in different measures of non-Markovianity [27, 77, 78]. It is related to the shape of the correlation function, which is the Fourier transform of the thermal spectral density and therefore depends on the occurence of sharp peaks leading to a long oscillatory decay of $C(t)$ and thus a long memory timescale. This strong interaction between the system and the baths requires efficient non-Markovian approaches and is dealt with the HEOM method. The key point is the expression of the correlation function of each bath b as a sum of $n_{cor,b}$ decay modes associated to the poles of the thermal spectral density (poles of the spectral density and of the Bose function also called Matsubara frequencies)

$$C_{t/c}(t) = \sum_{k=1}^{n_{cor,t/c}} \alpha_{t/c,k} e^{i\gamma_{t/c,k}t}. \qquad (10)$$

The HEOM method is well documented in the litterature [38, 40, 41, 53, 56, 79–84]. We adapt the HEOM algorithm by using a particular definition of the complex conjugate in which the rates remain the same in both expressions

$$C_{t/c}^*(t) = \sum_{k=1}^{n_{cor,t/c}} \tilde{\alpha}_{t/c,k} e^{i\gamma_{t/c,k}t}. \qquad (11)$$

Analytical expressions of the α_k, $\tilde{\alpha}_k$ and γ_k are given in references [76] and [85]. We summarize the operational equations in Appendix A, paying a particular attention to the backward propagation used in OCT. The corresponding expressions in the TT representation are given in appendix B.

Methods similar to HEOM operate by tracing out the bath degrees of freedom. However, even if the vibrational dynamics is not completely resolved, important information pertaining to the bath is available, for instance heat current or fluxes [81, 82, 86, 87]. The extraction and visualization of the time dependent thermal probability distributions $P_m(X_b, t)$ of each collective mode $b = t, c$ in each electronic state m is an interesting tool to analyze non–Markovian dynamics [70, 88]. $P_m(X_b, t)$ is expanded in the basis set of the eigenfunctions of the Ornstein–Uhlenbeck operator of the stochastic Liouville equation

$$P_m(X_b, t) = \sum_l a_{m,b,l}(t)\Phi_l(X_b) \qquad (12)$$

with $\Phi_l(X_b) = \frac{1}{\sqrt{2\pi}\sqrt{2^l l!}} H_l\left(X_b/\sqrt{2C_b(0)}\right) e^{-\frac{X_b^2}{2C_b(0)}}$ where the Hermite polynomials are weighted by a temperature dependent factor via the initial value of $C_b(t)$, which is the integral of the thermal spectral density. The computation may require HEOM at a high level when the distribution is far from the equilibrium Gaussian distribution. The expression of the $a_{m,b,l}(t)$ coefficients is given in Appendix A.

In particular, this first moment providing the average position of the coupling effective mode in each electronic

state $\langle X_b^m \rangle$ is obtained from the auxilliary density operators (ADO) of the first level for each bath

$$\mathbf{B}_b(t) = -\sum_\mathbf{n} \rho_\mathbf{n}(t) \qquad (13)$$

where the sum runs over all the collective index $\mathbf{n}$ for which $\sum_k n_{k,b} = 1$ with $b = t$ or $b = c$ respectively. The average in each electronic state is then given by the corresponding diagonal element

$$\left\langle X_b^{(m)} \right\rangle = \frac{1}{D_{0b}^{(m)}} (\mathbf{B}_b)_{mm} \qquad (14)$$

where D_{0b} is given by $D_{0t/c}^2 = (2/\pi) \int_0^\infty J_{t/c}(\omega)\omega d\omega$. This average is an interesting information about the vibrational relaxation and the evolution towards equilibrium. By expressing all the density matrices in Eq.(13) in the basis set of the localized diabatic states $D_{L/R}$ via the transformation matrix U given in Eq.(7), one gets the average position in each left or right diabatic wells showing the dissymmetry of the damped wave packet when the superposition $|\pm\rangle = (|S_1\rangle \pm |S_2\rangle)/\sqrt{2}$ is created. The electronic dissymmetry is estimated by the following parameter:

$$\Delta_X = \frac{1}{t_{lim}} \int_0^{t_{lim}} \left(\left\langle X_c^{(D_R)} \right\rangle + \left\langle X_c^{(D_L)} \right\rangle \right) dt \qquad (15)$$

where t_{lim} has been fixed at 100 fs in this application.

The HEOM equations summarized in Appendix A are propagated at $T = 298K$ by the Cash-Karp-Runge-Kutta algorithm [45] by a home-made parallelized fortran code. In Section V D we explore the implementation referring to the Tensor-Train approach. The HEOM equations adapted to this formulation are given in Appendix B. The propagation in the TT representation is made by the projector-splitting KSL scheme [48, 89, 90], designated by the three letters given to the three steps of the symmetrized splitting of second-order scheme also implemented in the ttpy package (`tt.ksl.ksl`) [91]. The number of matrices for K decay modes (Eq.(A2)) is then $N = \frac{(L+K)!}{L!K!}$. In the TT approach, n_{max} is the same for each mode leading to a larger number of matrix $N' = n_{max}^K$. The representation in TT is expected to reduce the storage resources (see Appendix B).

IV. FIELD DRIVEN DYNAMICS

Our objective is the depletion of the initial ground state and the creation of a coherent superposition of the excited states $|\pm\rangle = (|S_1\rangle \pm |S_2\rangle)/\sqrt{2}$. States $S_1(1B_2)$ and $S_2(2A_1)$ are excited by orthogonal transition dipole moments $\mu_y = 3.96$ ea_0 and $\mu_z = -1.83$ ea_0 respectively, the axes being defined in Fig.1. The molecule is in the plane Oyz orthogonal to the propagation direction Ox of the electromagnetic waves, as indicated in Fig.1. The time-dependent system Hamiltonian becomes $H_S(t) =$

$H_S + V(t)$ where the interaction with the electromagnetic field $\vec{\mathcal{E}}(t)$ is written in length gauge and within the dipole approximation. In a V-type system at frozen equilibrium geometry, the superposition could be prepared by two pulses with orthogonal polarizations and integrated Rabi frequencies equal to $\pi/\sqrt{2}$ in the absence of interference with another bright state. This has been shown for pulses of duration τ and sine square envelopes $\mathcal{E}_{y/z}(t) = \mathcal{E}_{0,y/z}\sin^2\left(\frac{\pi t}{\tau}\right)\cos\left(\omega_{y/z}t + \phi_{y/z}\right)$[63]. The maximum amplitudes are then given by $\mathcal{E}_{0,y/z} = \sqrt{2}\pi/(\mu_{y/z}\tau)$. When the pulses have the same duration, the field amplitudes are then in the inverse ratio of the dipole transition moments. However, for ultrashort pulses with one or two optical cycles, one must ensure a zero-area laser pulse [92, 93]. The field

$$\mathcal{E}_{y/z}(t) = -\frac{\partial \mathcal{A}_{y/z}(t)}{\partial t} \quad (16)$$

is then derived from the vector potential $\mathcal{A}_{y/z}(t) = \left(\frac{\mathcal{E}_{0,y/z}}{\omega}\right)\sin^2\left(\frac{\pi(t-t_i)}{\tau}\right)\sin\left(\omega(t-t_i) + \phi\right)$, where t_i is the initial time of the pulse.

The best superposition would be obtained by ultrashort pulses to fight against the decoherence induced by the baths. However, the spectral band should not exceed 0.25 eV to avoid any contamination with neighboring states. We therefore focus on pulses of some tens of femtoseconds during which interaction with the vibrational motions occurs. The first strategy involves positive or negative chirp pulses with a linear variation of the carrier frequency. For commodity, we introduce a factor f that remains close to one and the time dependent frequency is expressed by:

$$\omega(t) = \frac{\omega_{y/z}}{f} - \frac{(\omega_{y/z}/f) - f\omega_{y/z}}{\tau}t \quad (17)$$

where $\omega_{y/z}$ is the carrier frequency in resonance with the two transitions. The chirp rate $\omega' = \left[(\omega_{y/z}/f) - f \times \omega_{y/z}\right]/\tau$ is positive or negative according to $f > 1$ or $f < 1$.

In a second step, the best chirped pulses are taken as guess fields for optimization by OCT [42, 94]. The optimal field is built iteratively to maximize the cost functional also called performance index or objective index

$$I = \mathcal{R}_e(Tr\left[\rho^{\dagger}(\tau)\rho_{target}\right]) \quad (18)$$

at a final time τ with constraints to restrain the field intensity and to fulfill the master equation at any time. The corresponding Lagrange multipliers are denoted α and $\chi(t)$ respectively. The optimal field is obtained from the system matrix density propagated by the master equation with initial condition $\rho(t=0) = \rho_{ini}$ and from the Lagrange multiplier propagated with a final condition $\chi(\tau) = \rho_{target}$. The HEOM equations adapted for forward or backward propagations are given in the Appendix A and the corresponding TT representation in Appendix B. The field at each iteration k is obtained

by $\varepsilon^{(k)} = \varepsilon^{(k-1)} + \Delta\varepsilon^{(k)}$ where $\Delta\varepsilon^{(k)}$ is estimated by

$$\Delta\varepsilon(t) = \frac{1}{\alpha}\Im m\left\{Tr\left(\rho(t)\chi(t)\right)Tr\left(\chi(t)\left[\sum_p \mu_p, \rho(t)\right]\right)\right\} \quad (19)$$

where $p = y, z$ here [42].

V. RESULTS

A. Field free case

Figure 3 compares the field free dynamics with the full or the truncated spectral density (see Fig.2) by retaining only the highest frequency region for the two baths around 2360 ccm^{-1} (denoted 1L), the two highest peaks by adding those around 1700 c cm^{-1} (2L) and the full density (3L). This is the so-called ideal case when the initial condition is the superposition

$$|+\rangle = (|S_1\rangle + |S_2\rangle)/\sqrt{2} \quad (20)$$

corresponding to a population in the right side D_R. We compare the populations of the excited states $P_{S_1}(t)$ and $P_{S_2}(t)$ (Fig.3(a)), the average position of the coupling mode in the localized D_L and D_R states (Fig.3(b)) and the modulus of the coherence $|\rho_{S_1 S_2}(t)|$ (Fig.3(c)). The coherence

$$\rho_{S_1 S_2}(t) = \rho^*_{S_2 S_1}(t) \quad (21)$$

is the off-diagonal element corresponding to the two excited states denoted S_1 and S_2 of the system reduced density matrix

$$\rho(t) = Tr_B\left[\rho_{tot}(t)\right], \quad (22)$$

which is the trace over the bath modes of the full density matrix. In the target state (Eq.(20)) the coherence is $|\rho_{S_1 S_2}| = 0.5$. During the first ten femtoseconds, dynamics are dominated by the high frequency mode. After this early relaxation, the population exchange is reduced when the lower frequency around 1700 c cm^{-1} is considered. The modifications induced by the lowest frequency region are less significant and we adopt a compromise by retaining two peaks for each bath (2L) in order to reduce the computational cost. Indeed, the partition adopted here leads to a very high system-bath coupling demanding a high level in the HEOM propagation [69, 70]. HEOM is carried out at level 12 without Matsubara terms in the correlation function. Retaining only two Lorentzians per bath (2L) involves 1.3×10^5 matrices versus 2.7×10^6 matrices in the 3L model. In the field free case, the thermal equilibrium populations of the excited manifold are reached in 250 fs. The final populations are 0.39 for S_2 and 0.61 for S_1. We have verified that the equilibrium populations are the same for any intial excited state. These values do not correspond to a thermal Boltzmann mixture since the ground state is not coupled by non-adiabatic couplings with the excited states and the radiative decay is neglected. When
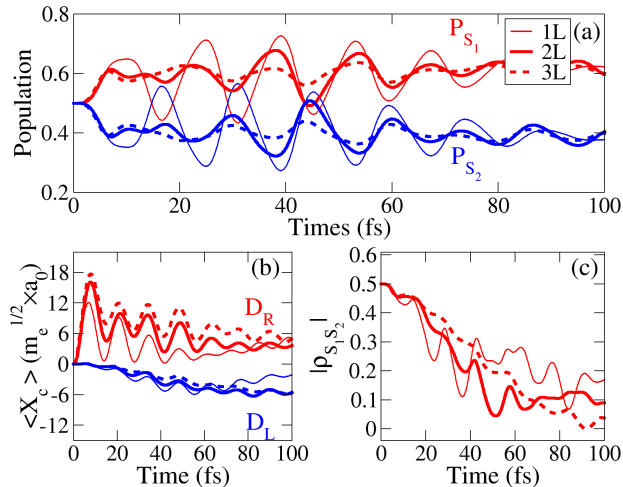
Figure 3. Field free so-called ideal case where the system is prepared in the superposed state $|+\rangle = (|S_1\rangle + |S_2\rangle)/\sqrt{2}$. Comparison of the dynamics with three spectral density models by retaining for each bath the highest frequency peak (1L, displayed in thin solid line), the two highest frequency peaks (2L, displayed as thick solid line) and the full density (3L, displyed in dashed line) (see Fig.2). Panel (a): Population in the excited electronic states S_1 (red) and S_2 (blue); panel (b): average position of the coupling mode in the localized diabatic states D_R (red) and D_L (blue); panel (c): modulus of the electronic coherence between the two excited states (Eqs.(21) and (22)).

Figure 4. Distributions $P_{D_L}(X_c,t)$ and $P_{D_R}(X_c,t)$ of the coupling collective mode in the localized excited states (model 2L). Panels (a) and (b): ideal case with the initial condition $|+\rangle = (|S_1\rangle + |S_2\rangle)/\sqrt{2}$ corresponding to a population in the right site D_R; panels (c) and (d): excitation from the ground state by two polarized pulses of 10 fs and amplitudes satisfying the $\pi/\sqrt{2}$ condition. The colorbar gives $P \times 10^2$.

we describe the excitation by laser pulses in the following sections, the population at equilibrium are different when the ground state is not completely depleted. The coherence decays in about 100 fs and the dissymmetry remains during the same period before leading finally to an equilibrium symmetric distribution in each well. The full distribution $P_{D_L}(X_c,t)$ and $P_{D_R}(X_c,t)$ (Eq.(12)) of the coupling mode in the D_L and D_R states is given in figures 4 (a) and 4 (b). This requires performing HEOM at least at level 15 to converge the expansion of Eq.(12). For this ideal case, the right side is populated and the oscillation persists during 40 fs before the transition towards the left side. For a simple statistical mixture with equal weights of the two states and no coherence, the population is always identical in both localized states.

B. Chirped laser pulses

Figures 4(c) and 4(d) give the distributions $P_{D_L}(X_c,t)$ and $P_{D_R}(X_c,t)$ when the system is initially in the ground electronic state with the vibrational baths at thermal equilibrium at the equilibrium geometry and excited by two polarized pulses along y or z with $\tau = 10$ fs and amplitudes satisfying the $\pi/\sqrt{2}$ rule. When the system is excited by the pulses, one has a first delay of about 5fs during the depopulation of the ground state before observing a notable density in the right side and the symmetry breaking has a lifetime shorter than in the field free ideal case.
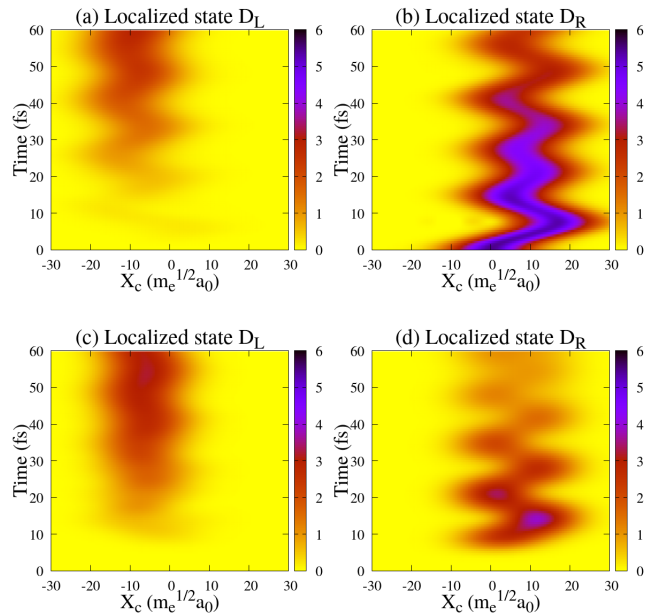
The first control against the decoherence during the interaction with the field is done by chirped pulses. For different pulse durations τ, the amplitudes of the two pulses are fixed by the $\pi/\sqrt{2}$ rule and we impose a positive or negative frequency chirp with a rate fixed by the f factor (Eq.(17)). The efficiency is measured by the dissymmetry parameter Δ_X (Eq.(15)) presented in figure 5. $\Delta_X = 2.30\ m_e^{1/2}a_0$ for the ideal case. A negative value does not mean that the initial localization is not on the right side but that later transitions may induce large oscillation in the left side. Whatever the sign, a non-zero value confirms the existence of a dissymmetry linked to a residual coherence. The positive chirp increases the dissymmetry only for τ in the range 10-35 fs. For longer pulses (35-50 fs) that exceed the coherence lifetime of the ideal case, the efficiency is very weak in the absence of any chirp ($f = 1$). Negative chirps slightly improve the result.

In the following subsection, we select three pulses of 50, 15 and 10 fs with the chirp factor f giving the maximum absolute value of Δ_X. The first is longer than the decoherence time of the ideal case and the second one corresponds to the vibrational period of the effective coupling mode. These pulses are guess fields for an optimization by OCT to check which kind of restructuring is finally obtained.
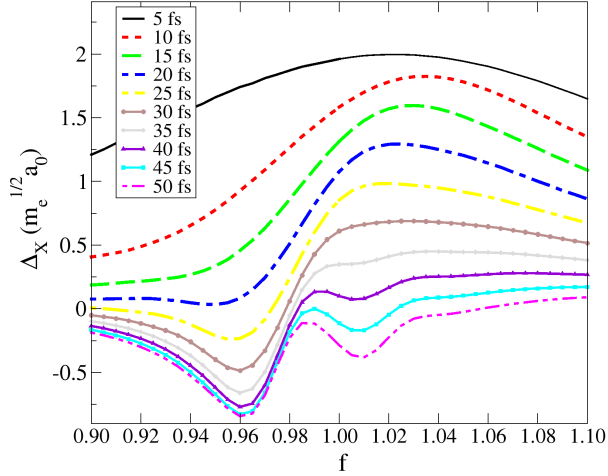
Figure 5. Electronic dissymetry Δ_X (in $m_e^{1/2}a_0$) defined by Eq.(15) for two polarized pulses along y or z with positive ($f > 1$) and negative ($f < 1$) chirps. The f factor determining the chirp rate is given in Eq.(17).
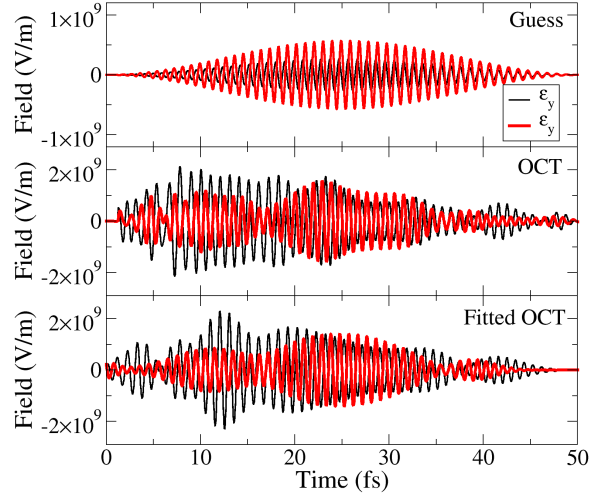

Figure 6. Optimal fields $\mathcal{E}_y$ (black thin line) and $\mathcal{E}_z$ (thick red line) obtained when the guess fields are the pulses of 50 fs with a negative chirp with $f = 0.962$ (Eq.(17)). The fit is obtained with six Gaussian pulses for each polarisation. The parameters are given in the Supplemental Material.

C. Optimal control

The target reduced density matrix ρ_{target} at the end of the pulses τ is the one corresponding to the superposition $|+\rangle = (|S_1\rangle + |S_2\rangle)/\sqrt{2}$ with zero population in the initial equilibrium ground state. Our strategy is to let OCT optimize the y and z fields on a time grid. The objective index I (Eq.(18)) is never 100% (i.e. $|\rho_{S_1S_2}| = 0.5$) because we limit the field amplitude to an upper value of 10^{-2} a.u. (5.1422×10^9 Vm^{-1}) corresponding to an intensity of 3.51×10^{12} Wcm^{-2}. The OCT fields obtained from the 50, 15 and 10 fs chirped guess fields and their fits are presented in figures 6, 8 and 10 respectively. We then fit the optimal fields for each polarization with a sequence of N_G simple Gaussian pulses with central time T_M

$$\mathcal{E}_{y/z}^{Fit}(t) = \sum_i^{N_G} \varepsilon_{0_i} e^{-\frac{(t-t_{M_i})^2}{2\sigma_i^2}} \cos(\omega_i(t - t_{M_i})). \quad (23)$$

The optimally fitted parameters $\varepsilon_{0_i}, t_{M_i}, \sigma_i, \omega_i$ are given in the Supplemental Material. We use Trust Region Reflective algorithm (TRR) of the python module scipy.optimize to fit the optimal fields. The algorithm uses non-linear least squares to fit data to a functional form [95, 96]. In each case, OCT strongly reshapes the simple chirped pulses and suggests a sequence of pulses with nearly the same delay for both polarisations. The RMS of the fits is very good. It is given with all the parameters in the Supplemental Material. The fitted fields with a pulse sequence are not fully identical but they retain the main features of the dynamics as seen in figures 7, 9 and 11 where dynamics are compared .

(i) In the 50 fs case, the penalty factor is $\alpha = 5 \times 10^3$ (Eq.(19)). The performance index (Eq.(18)) after 50 iterations is $I = 84\%$ providing a coherence of 0.34. Modifying α only influences the rate of convergence but the

optimal coherence never exceeds about 0.35 but nevertheless remains three time higher than the value given by the guess field. The creation of the coherence is more difficult for long pulses. However, the dissymetry of the average value of the coupling mode in both sides is more striking for the long pulses. OCT notably improves the depletion of the ground state, the residual population being about 0.05 *versus* 0.62 with the chirped pulse. The OCT field consists of six pulses (around 5, 10, 17 and 29 fs) roughly corresponding to two pulses per vibrational period (14 fs).

(ii) In the 15fs case, with $\alpha = 1 \times 10^4$ one gets $I= 89\%$ and a coherence of 0.42 after 150 iterations. The creation of the coherence is better for the short pulses; i.e. 0.42 as compared to 0.28. The residual population in the ground state is about 0.05 *versus* 0.38. The reshaping is particularly striking in this case leading to two main pulses for each polarisation.

(iii) In the 10 fs case, $\alpha = 2 \times 10^4$, $I= 87\%$ with a coherence of 0.43 *versus* 0.29 after 30 iterations. The improvement is less sepctacular. Even for this short duration, OCT reshapes the field suggesting a central shorter pulse of higher amplitude in a train of three pulses.

In all the previous examples, the simultaneous addressing of the two electronic states by the two polarizations is maintained in the OCT fields. To check the stability of this result, we also use a sequence of pulses with the two alternating polarizations and the same duration. Without bath, a first $\pi/2$ pulse polarized along z makes a superposition of the ground and one excited state. Then a π pulse polarized along y in resonance with the second transition inverts the population of the ground and the second excited state. This guess field is less efficient than the simultaneous chirped pulses.
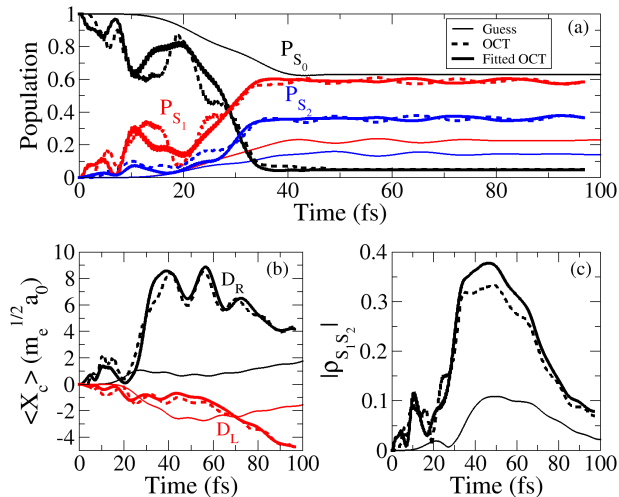
Figure 7. Comparison between the dynamics driven by the chirped y and z pulses of 50 fs with $f = 0.962$ (Eq.(17)), the optimal pulses obtained with these guess fields and the sequence of six Gaussians pulses fitting each OCT pulse. Panel (a): Population in the ground S_0 (black) and the excited electronic states S_1 (red) and S_2 (blue); panel (b): average position of the coupling mode in the localized diabatic states D_R (black) and D_L (red); panel (c): modulus of the electronic coherence between the two excited states (Eqs.(21) and (22)).
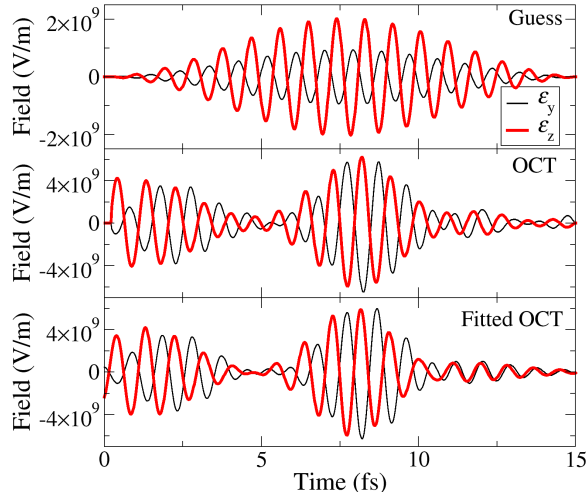

Figure 9. Comparison between the dynamics driven by the chirped y and z pulses of 15 fs with $f = 1.03$ (Eq.(17)), the optimal pulses obtained with these guess fields and the sequence of three Gaussians pulses fitting each OCT pulse. Panel caption as in Fig.(7).

Figure 8. Optimal fields $\mathcal{E}_y$ and $\mathcal{E}_z$ obtained when the guess fields are the pulses of 15 fs with a positive chirp with $f = 1.03$ (Eq.(17)). The fit is obtained with three Gaussian pulses for each polarisation. The parameters are given in the Supplemental Material.

Figure 10. Optimal fields $\mathcal{E}_y$ and $\mathcal{E}_z$ obtained when the guess fields are the pulses of 10 fs with a positive chirp with $f = 1.04$ (Eq.(17)). The fit is obtained with three Gaussian pulses for each polarisation. The parameters are given in the Supplemental Material.

The interesting result is that OCT reshapes the fields by mixing the polarization from the beginning. This is illustrated for a sequence of total duration 15 fs in the Supplemental Material.
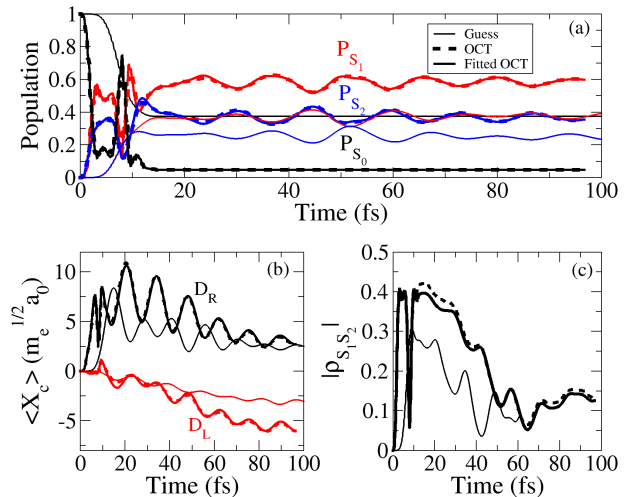
D. OCT by Tensor Trains

Finally, in the 10 fs case (see Fig.(11)) we compare the simulations with the usual Cash-Karp-Runge-Kutta (denoted HEOM) and the TT implementation (denoted TT-HEOM) described in Appendix B. For these fast dynamics, the behavior is nearly similar when the spectral densities are approximated by one or two Lorentzians, namely the models 1L or 2L discussed above (see figure 3). In the 1L case, the optimization is made in 50 iterations with $\alpha = 2 \times 10^4$. In the 2L case, we consider 30 iterations with $\alpha = 1 \times 10^4$ (α is decreased to

Figure 11. Comparison between the dynamics driven by the chirped y and z pulses of 10 fs with $f = 1.04$ (Eq.(17)), the optimal pulses obtained with these guess fields and the sequence of three Gaussians pulses fitting each OCT pulse. Panel caption as in Fig.(7).
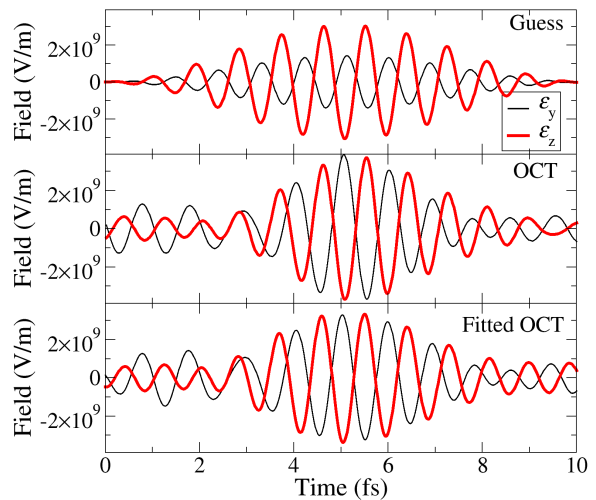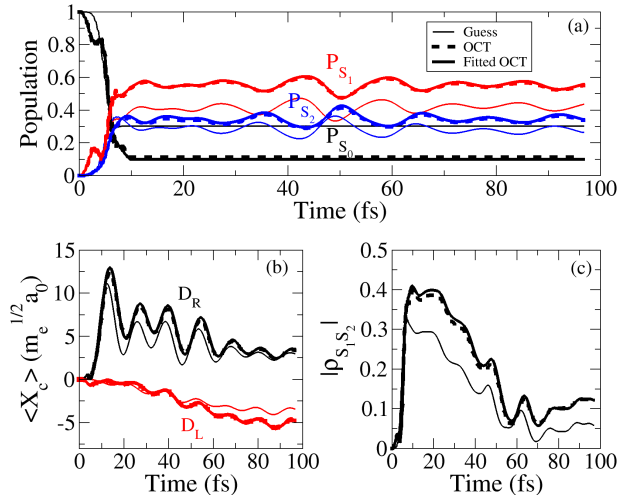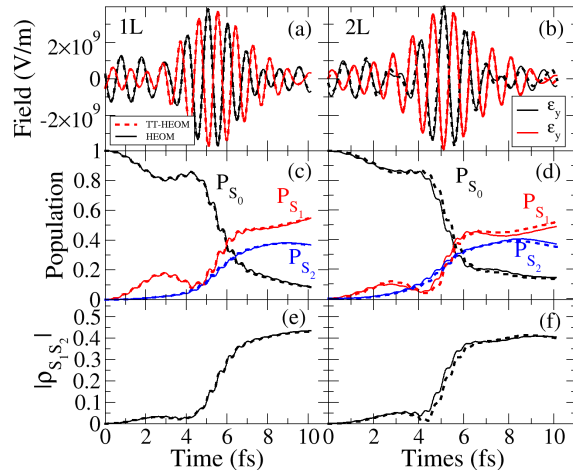

Figure 12. Comparison between the dynamics performed by the adaptative Runge Kutta method (HEOM) and TT simulation (TT-HEOM) with 10 fs pulse duration when the spectral densities are approximated by one (1L) or two (2L) Lorentzians. The HEOM level is 8. OCT is driven in 50 iterations with $\alpha = 2 \times 10^4$ for 1L and 30 iterations with $\alpha = 1 \times 10^4$ for 2L.

speed up the optimization rate). The HEOM level is 8 in each example. Dynamics are compared in figure 12, left panels (a,c,e) for 1L and right panels (b,d,f) for 2L. As one could notice, adaptative Runge Kutta method HEOM, displayed in solid thin lines, and TT simulations in dotted line give roughly the same fields, same populations, and same coherences. For both cases 1L and 2L, we obtain similar encouraging results. However, it is difficult to ensure a good convergence when the spectral density presents several peaks. The ordering of the modes may be an important factor influencing the efficiency of Time Dependent Variational Principle (TDVP) methods [97]. Further improvements are currently underway to consider the reorganization of the modes [72, 98], rank adaptative methods [37, 56, 99–101] or hierarchical tensor train approach [55].

VI. CONCLUSION

This work addresses the laser control of the electronic symmetry breaking inducing a localization and a transitory oscillation on a given side of a symmetric dimer. The target initial electronic state is a superposed state of two nearly degenerate bright states coupled through a conical intersection. An initial superposition with equal weigths of the delocalized excited adiabatic states in phase (plus sign) or out of phase (minus sign) corresponds to a localized diabatic state with electronic density on one or the other side of the symmetric dimer. Preparing a superposition means maintaining the electronic coherence during the control process. Ultra-short pulses with broad energy band are a priori more favorable but they may interfere with additional bright states. We mainly consider control extending on some

tens of femtoseconds to ensure a width of about 0.25 eV. Then decoherence occurs during the pulses due to vibrational motions.

The control targets are the highest possible population in the excited manifold and the highest possible coherence (0.5 in our case) corresponding to the expected superposition, which induces the maximum dissymetry. Based on experimental constraints concerning pulse shaping (frequency chirping rate, leading intensities), and the property of the V-type system with orthogonal transition dipole moments, we consider three steps. (i) We examine guess fields inspired from mechanisms whose efficiency is well known in absence of baths: simultaneous pulses linearly polarized along orthogonal directions with negative or positive linear chirps, and fulfilling for their amplitudes the $\pi/\sqrt{2}$ time integration condition, or sequence of $\pi/2$ and π pulses with alternative polarization. (ii) We use these guess fields to initiate an optimal control scheme to see the suggested reshaping. (iii) We check the robustness of such fields by fitting them with a sequence of simple Gaussian pulses.

It is worthy to note that the dissymetry towards the right or the left side may be easily reversed by changing the sign of the pulse with polarization z coupling to state S_2 through μ_z. This phase inversion generates the superposed state with the minus sign and changes the populated localized side. This is verified for the guess field and for the corresponding OCT field.

TT is a very promising approach for solving HEOM as it tackles the dimensionality curse with respect to the necessary memory space. Moreover, TT appraoch is a background for future implementation of deap learning algorithms [98]. We have explicited the TT representa-

tion of the HEOM equations for OCT. However, it turns out that the present molecular system is particularly demanding since the electron-nuclei partition leads to strong system-bath coupling and a high hierarchy level with the ensuing large number of ADOs and a structured spectral density with at least two important peaks per nath. We face several numerical difficulties and instabilities when addressing structured spectral densities. An adaptive rank is necessary during the propagation. We have improved the results by a mixed strategy including steps with the Runge-Kutta algorithm in the variational time dependent KSL procedure to increase the ranks. Further developments with other adaptive methods are on going [99, 100].

As the molecular system is of moderate size, in principle, full quantum dynamics with the LVC model could be performed by the variational ML-MCTDH (Multi-Layer Multi-configuration Time-Dependent Hartree [102] with thermal average over initial conditions. Similar results are expected for very short laser pulses, mainly before the so-called Zeno time [103]. However, it is not clear whether the thermalization is treated on an equal foot in wave packet with initial time average and in the open quantum system. Noise could also be introduced in a stochastic time-dependent Schrödinger equation with an improved treatment of the thermalization [104].

On general grounds, one observes that OCT suggests interesting strategies that could eventually be quite diffrent from an intial guess. For the very smooth simultaneous y and z chirps at resonance, OCT reshapes the fields in a sequence of few pulses of 5 or 10 fs, slightly off-resonance and addressing again simultaneously the two excited states. When the guess is a sequence of π and $\pi/2$ pulses addressing successively the two states, OCT confirms our first strategy based on simultaneous use of the two polarizations by mixing from the very beginning the y and z polarizations. OCT suggests the number of individual pulses and the simultaneous use of the polarisations. In this work, we have fitted Gaussian pulses on the OCT fields. However, the OCT fields do not fully reach the target. The following step in prospect is optimizing the parameters (amplitude, frequency, central position and width) imposing only the number of pulses suggested by OCT.

SUPPLEMENTARY MATERIAL

The supplemental material gives the Cartesian coordinates of the atoms at the ground state equilibrium geometry computed at the CAM-B3LYP/6-31+G* level of theory. It gives the gradients of the discrete LVC model and the parameters of the Tannor-Meier fit (Eq.(9)) of the spectral densities. We also gather the parameters of the Gaussian pulses fitting the OCT fields. An important part is devoted to a pedagogical survey showing the way the super-operators involved in the TT-HEOM formalism are written as illustrated on a simple case.

DATA AVAILABILITY

The data that support this study are available on request from the authors.

Appendix A: HEOM equations for forwards and backwards propagation

The non-Markovian master equation for the reduced density matrix of the system $\dot{\rho}(t) = -\frac{i}{\hbar}Tr_B\left[\hat{H}, \rho_{tot}(t)\right]$, where $\rho_{tot}(t)$ is the full density matrix, is solved by a time local system of coupled equations among auxiliary matrices arranged in a hierarchical structure. Each auxiliary matrix has the dimension of $\rho(t)$ and is labelled by a collective index

$$\mathbf{n} = \{n_1, \cdots, n_K\} \tag{A1}$$

specifying the phonon occupation number of each decay mode in each bath b,

$$K = \sum_b^{N_B} n_{cor,b} \tag{A2}$$

where N_B is the number of baths, here $N_B = 2$ and $b = t, c$ (see Eq.(10)). The system density matrix has the index $\mathbf{n} = \{0, \cdots, 0\}$. Matrices with an occupation number rising or descending by one unit are the only ones connected in the hierarchy.

The non-Markovian forward equation of OCT is an equation with initial condition, which may be written $\dot{\rho}(t) = L_S\rho(t) + \int_0^t K(t,t')\rho(t')dt'$. The corresponding coupled equations of HEOM with correlation functions (Eqs.(10) and(11)) and with $\hbar = 1$ are:

$$\dot{\rho}_{\mathbf{n}} = L_S\rho_{\mathbf{n}} + i\sum_b^{N_B}\sum_{k=1}^{n_{cor,b}} n_{k,b}\gamma_{k,b}\rho_{\mathbf{n}} - i\sum_b^{N_B}\left[S_b, \sum_{k=1}^{n_{cor,b}}\rho_{\mathbf{n}_{k,b}^+}\right]$$
$$- i\sum_b^{N_B}\sum_{k=1}^{n_{cor,b}} n_{k,b}\left(\alpha_{k,b}S_b\rho_{\mathbf{n}_{k,b}^-} - \tilde{\alpha}_{k,b}\rho_{\mathbf{n}_{k,b}^-}S_b\right) \tag{A3}$$

where $L_{S\bullet} = -i[H_S(t), \bullet]$ and the α_k, $\tilde{\alpha}_k$, γ_k parameters are defined in Eqs.(10) and (11). The analytical expressions as a function of the spectral density parameters are given in references [76, 85]. The S_b operators are defined in section III. The rising $\mathbf{n}_k^+ = \{n_1, \cdots, n_k + 1, \ldots, n_{n_{cor}}\}$ and descending $\mathbf{n}_k^- = \{n_1, \cdots, n_k - 1, \ldots, n_{n_{cor}}\}$ matrices are those for which

the occupation number differs by one unit in the hierarchy $n_k \to n_k \pm 1$. The initial condition is assumed to be factorized $\rho_{tot}(t_0) = \rho(t_0)\rho_{eq}$ where ρ_{eq} is the Boltzmann equilibrium distribution at the chosen temperature. The separable initial condition is justified because the vibrational bath is initially at equilibrium and the electronic system is in the ground state decoupled from the excited manifold. It may also be valid in the case of an ultra-fast Franck-Condon excitation.

The Lagrange multiplier of OCT is propagated with a final condition $\chi(t_f) = \rho_{target}$ at the time $t = t_f$ (end of the laser pulse). The non-Markovian equation with a final equation involves a different memory term $\dot{\chi}(t) = L_S\chi(t) - \int_t^{t_f} K^\dagger(t,t')\chi(t')dt'$ corresponding to the following coupled equations:

$$\dot{\chi}_\mathbf{n} = L_S\rho_\mathbf{n} - i\sum_b^{N_B}\sum_{k=1}^{n_{cor},b} n_{k,b}\gamma_{k,b}\rho_\mathbf{n} - i\sum_b^{N_B}\left[S_b, \sum_{k=1}^{n_{cor},b}\rho_{\mathbf{n}_k^+}\right]$$

$$+ i\sum_b^{N_B}\sum_{k=1}^{n_{cor},b} n_k\left(\alpha_{k,b}\rho_{\mathbf{n}_k^-}S_b - \tilde{\alpha}_{k,b}S_b\rho_{\mathbf{n}_k^-}\right) \tag{A4}$$

In practice they are solved backwards starting from $\chi(t_f) = \rho_{target}$ and all the auxiliary matrices set equal to zero. The factorized condition is less obvious than for the forward preparation but the final condition does not correspond to a new equilibrium state of the baths.

For each electronic state m the coefficients $a_{m,b,l}(t)$ in the expansion of the time dependent thermal probability distributions $P_m(X_{t/c}, t)$ of each collective mode (Eq.(12)) are the corresponding diagonal element of a matrix built from the auxiliary operators $\mathbf{A}_{b,l}(t) = \frac{(-1)^l}{\sqrt{l!C_b^l(0)}}\sum_\mathbf{n}\frac{l!}{\Pi n_{k,b}}\rho_\mathbf{n}(t)$ where the sum $\sum_k n_{k,b} = l$ [70, 81, 82] runs over the index $\mathbf{n}$ for which the partial level of bath b is equal to l.

Appendix B: Tensor trains

As already suggested by Shi [53–55] and later by Borelli [56], we investigate solving the hierarchical equations of motion (Eqs.(A3) and (A4)) by using the so-called Tensor Train (TT) decomposition (also referred to as matrix product state (MPS) in the quantum physics community [37, 46–50, 52, 97, 105]). The usual truncation of the hierarchy retains all the ADOs up to a level L so that the sum of the occupation number is equal to L.

1. Tensor train representation of the density matrices

HEOM formalism relies on a set of auxiliary matrices which is basically a multidimensional array $\rho_\mathbf{n}$ where $\mathbf{n}$ and K are defined in Eqs.(A1) and (A2) respectively. Instead of considering a set of density matrices of dimension $n \times n$ with n being the number of states in the
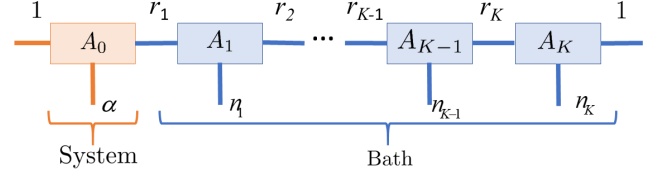

Figure 13. Tensor train decomposition schematization. A_k are the cores of the tensor, α runs from 1 to n^2 where n is the number of states in the system and n_k is the index for each decay mode that runs from 0 to n_{max}.

system Hamiltonian H_S, we flatten each matrix as a n^2 vector without loss of generality. This "vectorized" density matrix will be denoted $\bar{\rho}_\mathbf{n}$ and each of its element α ($\alpha \in [1, n^2]$) written in TT-format as :

$$\bar{\rho}_\mathbf{n}^\alpha \approx \sum_{j_0}\sum_{j_1}\cdots\sum_{j_k}\cdots\sum_{j_{K+1}} A_0(j_0, \alpha, j_1)A_1(j_1, n_1, j_2)\cdots$$
$$A_k(j_k, n_k, j_{k+1})\cdots A_K(j_K, n_K, j_{K+1}) \tag{B1}$$

Here, j_k goes from 1 to r_k where r_k is the kth rank of the tensor (note that $r_0 = r_{K+1} = 1$ for dimensionality consistency). A_k are called cores and consist in arrays of dimension $r_k \times n_e \times r_{k+1}$ where $n_e = n^2$ for $k = 0$ and $n_e = n_{HEOM} = n_{max} + 1$ for $k \neq 0$ (n_{HEOM} is the hierarchy order) .

Tensor trains are often schematized as shown in figure 13 with the tensor network displaying a train shape where several cars are successively connected. Such decomposition is exact as long as the tensor ranks r_k grow without limitation. In practise, r_k are parameters during the simulation and one has to carefully check the convergence over them. Details on the mathematical background are not the scope of this article but they can be found in refs [47, 48, 51]. We heavily rely on the library ttpy developed in Python and Fortran by Oseledets and co-workers [91]. It provides a user-friendly interface to build tensor trains, convert matrices (`tt.matrix`) and vectors (`tt.vector`) in TT-format and deal with the algebra of basic arithmetic operations ($+, -,$etc) and Kronecker products (`tt.kron`) on TT-format objects.

To compute the system density matrix, we avoid a full expansion of $\bar{\rho}_\mathbf{n}^\alpha$ to overcome memory limitations. Instead, we make use of projectors in TT-format :

$$\mathcal{P}_\alpha = P_\alpha \otimes \prod_{j=1}^{K} V_j \tag{B2}$$

where P_α is a vector of dimension n^2 with elements $P_{\alpha,l} = \delta_{\alpha,l}$ and V_j a vector of dimension n_{HEOM} with elements $V_{j,1} = 1$ if $l = 1$ and $= 0$ if $l \neq 1$. Thus, the elements of the system density vector writes :

$$\bar{\rho}_{\mathbf{n}=\{0,\cdots,0,\cdots,0\}}^\alpha = \mathcal{P}_\alpha \cdot \bar{\rho}_\mathbf{n} \tag{B3}$$

2. Time evolution

We solve the dynamic problem by using the projector-splitting KSL scheme [48, 89, 90] implemented in the ttpy package (`tt.ksl.ksl`) [91]. To use this algorithm, one has to provide a single super-operator which acts on the full TT-converted vector $\bar{\rho}_{\mathbf{n}}$ (or $\bar{\chi}_{\mathbf{n}}$ in the case of backward propagation) representing all the auxiliary density operators such that:

$$\frac{d}{dt}\bar{\rho}_{\mathbf{n}} = \mathcal{L}\bar{\rho}_{\mathbf{n}} \tag{B4}$$

$$\frac{d}{dt}\bar{\chi}_{\mathbf{n}} = \mathcal{L}_b\bar{\chi}_{\mathbf{n}}. \tag{B5}$$

The Liouvillian super-operators $\mathcal{L}$ and $\mathcal{L}_b$ can be derived from the hierarchical set of equations of motions for both the forward (Eq.(B4)) and backward (Eq.(B5)) propagations. We provide below a summary of the essential equations to build these Liouvillian operators. It is noteworthy to mention that all the necessary arithmetic operations can be performed in TT-format.

a. Forward propagation

For the forward propagation, the associated Liouvillian (Eq.(B6) denoted in our case as a super-operator $\mathcal{L}$ writes :

$$\mathcal{L} = \mathcal{L}_S + \sum_{k'=1}^{K} \left(\mathcal{L}_{k'} + \mathcal{L}_{k'-} + \mathcal{L}_{k'+} \right) \tag{B6}$$

Here, $k' = (k, b)$ is a collective index which adresses both the index of the correlation function terms ($k \in [1, n_{cor,b}]$) (see Eq.(10)) and index of bath ($b \in [1, N_B]$). Each of the terms in Eq.(B6) can be further derived as Kronecker products of various operators. In the following expressions, I_n denotes the identity matrix with dimensions $n \times n$, $\otimes$ is a matrix Kronecker product for two matrices, $\otimes \prod$ is an ordered (from left to right) sequence of Kronecker products and $\delta_{l,m}$ is a delta Kronecker symbol ($\delta_{l,m} = 1$ if $l = m$; 0 if $l \neq m$).

The system Liouvillian writes:

$$\mathcal{L}_S = -i(H_S \otimes I_n - I_n \otimes H_S) \otimes \prod_{k''=1}^{K} I_{n_{HEOM}} \tag{B7}$$

The "damping" term is:

$$\mathcal{L}_{k'} = i\gamma_{k',t/c}I_{n^2} \otimes \prod_{k''=1}^{K} M_{k''} \tag{B8}$$

where $M_{k''} = I_{n_{HEOM}}$ if $k'' \neq k'$ and $M_{k'',lm} = (l - 1)\delta_{l,m}$ if $k'' = k'$ ($l, m \in [1, n_{HEOM}]$).

The superoperator connecting the ADOs with an upper layer in the hierarchy is:

$$\mathcal{L}_{k'+} = -i(S_{k'} \otimes I_n - I_n \otimes S_{k'}) \otimes \prod_{k''=1}^{K} M'_{k''} \tag{B9}$$

where $M'_{k''} = I_{n_{HEOM}}$ if $k'' \neq k'$ and $M'_{k'',lm} = \delta_{l+1,m}$ if $k'' = k'$ ($l, m \in [1, n_{HEOM}]$).

The superoperator connecting ADOs with a lower layer in the hierarchy is:

$$\mathcal{L}_{k'-} = -i(\alpha_{k',t/c}S_{k'} \otimes I_n - \tilde{\alpha}_{k',t/c}I_n \otimes S_{k'}) \otimes \prod_{k''=1}^{K} M''_{k''} \tag{B10}$$

where $M''_{k''} = I_{n_{HEOM}}$ if $k'' \neq k'$ and $M''_{k'',lm} = (l - 1)\delta_{l-1,m}$ if $k'' = k'$ ($l, m \in [1, n_{HEOM}]$).

Finally, for pedagogical purpose, we provide in the SM, a step-by-step through derivation of the superoperators with a simplified two-dimensional system, and a single tuning bath treated by HEOM at level 2.

b. Backward propagation

The very same procedure can be applied for the backward propagation. Thus, the backward Liouvillian $\mathcal{L}_b$ writes :

$$\mathcal{L}_b = \mathcal{L}_S + \sum_{k'=1}^{K} \left(-\mathcal{L}_{k'} + \mathcal{L}_{bk'-} + \mathcal{L}_{k'+} \right) \tag{B11}$$

where the superoperator acting on a lower layer is slightly modified as:

$$\mathcal{L}_{bk'-} = i(\alpha_{k',t/c}I_n \otimes S_{k'} - \tilde{\alpha}_{k',t/c}S_{k'} \otimes I_n) \otimes \prod_{k''=1}^{K} M''_{k''} \tag{B12}$$

One can check by expanding $\mathcal{L}$ (Eq.(B6)) and $\mathcal{L}_b$ (Eq.(B11)) that Eq.(B4) and Eq.(B5) are equivalent to Eq.(A3) and Eq.(A4) respectively.

Appendix C: List of abbreviations

We summarize the list of the abbreviations with the section of their definition.

HEOM Hierarchical Equations of Motion (Sec.I)

OCT Optimal Control Theory (Sec.I)

TT Tensor Train (Sec.I)

ML-MCTDH Multi-Layer Multi-configuration Time-Dependent Hartree (Sec.VI)

LVC Linear Vibronic Coupling (Sec.I)

TRR Trust Region Reflective algorithm (Sec.V C)

RMS Root Mean Square (Sec.V C)

TDVP Time Dependent Variational Principle (Sec.V D)

KSL name of an algorithm based on an integration scheme that successively updates three component matrices: K, S, and L [48, 89, 90] (Sec.III)

MPS Matrix Product State (Sec.B)

ADO Auxiliary Density Operator (Sec.III)

PPE Phenylene Ethynylene (Sec.I)

DFT Density Functional Theory (Sec.II)

TD-DFT Time Dependent Density Functional Theory (Sec.II)

CAM-B3LYP Coulomb Attenuated Method Becke,3-parameetr,Lee-Yang-Parr (Sec.II)

MECI Minimum Energy Conical Intersection (Sec.II)

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