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New strategy for optimal control of femtosecond pump-dump processes applicable to systems of moderate complexity

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Abstract. New pump-dump optimal control strategy applicable to the systems of moderate complexity has been developed which allows to drive the system to the desired objective in the ground state *via* electronically excited state. The strategy is based on the concept of the intermediate target in the excited state whose role is to select appropriate Franck-Condon window at a given time delay between pump and dump pulses in order to reach optimally the objective. The concept was applied on the isomerization process in Na_3F_2 employing our *ab initio* Wigner distribution approach. The pump and dump pulses have been found which suppress the radiationless transition through the conical intersection and drive the system *via* electronically excited state to the second isomer in the ground state with the maximal yield.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 31.15.Ar Ab initio calculations

1 Introduction

Recent developments of experimental pulse-shaping techniques have made possible to generate laser fields which are able to perform optimal control of molecular processes on the femtosecond scale [1–5]. Together with the optimal control theory [6–12] the field has been considerably advanced over past years. However, the extent to which optimal control can be achieved in the case of systems of increased complexity remains still an open question. There are two problems which arise here. The first one concerns the existence of the connective pathway between the initial state and the objective, which is not automatically guaranteed in the case of the multidimensional system when the objective is reached *via* a different electronic state with distinct features, and the second one is how the connective pathway can be found. Since our approach is based on the combination of Wigner distribution method and *ab initio* molecular dynamics in excited and ground electronic states [13–15], the analysis of the *ab initio* MD allows us to introduce the concept of the intermediate target in the excited state. It is defined as a localized ensemble corresponding to the maximum overlap between the forward propagated phase space density on the excited electronic state and backward propagated phase space density from the objective in the ground state. Defined in this way, the intermediate target ensures the connective pathway between the initial state and objective. Using this concept, we show on the example of the Na_3F_2 cluster that optimal pump and dump pulses can be found, which maximally populate the objective (second isomer) in the ground state and suppress radiationless transition through conical intersection [15].

2 The strategy for optimal control

We consider pump-dump control in the weak field second order perturbation theory [12,16,17] regime with two phase unlocked pulses of the form

$$\epsilon_{P(D)}(t) = E_{P(D)}(t)\exp\left(-\mathrm{i}\omega_{eg}t\right) + E^*_{P(D)}(t)\exp\left(\mathrm{i}\omega_{eg}t\right)$$

where $E_{P(D)}$ is a slowly varying envelope of the pump(dump) fields, and ω_{eg} is the difference between the energies of the minima of the excited and the ground state. The aim is to maximally populate the second isomer in the ground state at a given time delay t_f. The parameters which are involved in the optimization are the shapes of both pulses and the time delay between them. 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. $A(\Gamma)$ is defined as:

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

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which corresponds to the spatial localization of the phase space density with arbitrary distribution of momenta. After performing the variation of the functional

$$J(t_f) = A(t_f) - \lambda_P \int_0^{t_f} |E_P(t)|^2 \,\mathrm{d}t - \lambda_D \int_0^{t_f} |E_D(t)|^2 \,\mathrm{d}t. \tag{2}$$

The integral equations of the Fredholm type for the envelopes of the optimal pump and dump pulses are obtained:

$$\int_0^{t_f} \mathrm{d}\tau' \, M_P(\tau, \tau'; E_D) E_P(\tau') = \lambda_P E_P(\tau) \tag{3}$$

$$\int_0^{t_f} \mathrm{d}\tau' \, M_D(\tau, \tau'; E_P) E_D(\tau') = \lambda_D E_D(\tau), \tag{4}$$

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

$$\begin{aligned} M_P(\tau, \tau'; E_D) = \int\int \mathrm{d}^2\Gamma_0 \int_0^{t_f} \mathrm{d}\tau'' \int_0^{\tau''} \mathrm{d}\tau''' \\ \times A\left(\Gamma_g\left(t_f - \tau''; \Gamma_e\left(\tau''' - \tau; \Gamma_0\right)\right)\right) \\ \times \mathrm{e}^{\mathrm{i}(\omega_{eg} - U_{eg}(\Gamma_e(\tau''' - \tau; \Gamma_0))(\tau'' - \tau''')} \\ \times \mathrm{e}^{\mathrm{i}(\omega_{eg} - U_{eg}(\Gamma_0))(\tau - \tau')} \\ \times \rho_{gg}(\Gamma_0) E_D(\tau''') E_D^*(\tau'') \quad \tau \geq \tau', \end{aligned} \tag{5}$$

$$\begin{aligned} M_D(\tau, \tau'; E_P) = \int\int \mathrm{d}^2\Gamma_0 \int_0^{\tau'} \mathrm{d}\tau'' \int_0^{\tau''} \mathrm{d}\tau''' \\ \times A(\Gamma_g(t_f - \tau; \Gamma_e(\tau' - \tau''; \Gamma_0))) \\ \times \mathrm{e}^{\mathrm{i}(\omega_{eg} - U_{eg}(\Gamma_e(\tau' - \tau''; \Gamma_0))(\tau - \tau')} \\ \times \mathrm{e}^{\mathrm{i}(\omega_{eg} - U_{eg}(\Gamma_0))(\tau'' - \tau''')} \\ \times \rho_{gg}(\Gamma_0) E_P(\tau''') E_P^*(\tau'') \quad \tau \geq \tau', \end{aligned} \tag{6}$$

and Γ_e and Γ_g correspond to propagated excited and ground state ensembles. Since both of the equations are dependent on both pump and dump fields, their solution requires an iterative procedure which is computationally very demanding task for a system of moderate complexity. Our strategy is based on decoupling these equations by restricting the optimization to field envelopes in the fs regime. The steps which are involved are:

(i) In the zeroth step we 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. The zeroth order material response functions become then

$$\begin{aligned} M_P^{(0)}(\tau, \tau') = \int\int \mathrm{d}^2\Gamma_0 A(\Gamma_g(t_f - t_d; \Gamma_e(t_d - \tau; \Gamma_0))) \\ \times \mathrm{e}^{\mathrm{i}(\omega_{eg} - U_{eg}(\Gamma_0))(\tau - \tau')} \rho_{gg}(\Gamma_0); \quad \tau \geq \tau' \end{aligned} \tag{7}$$

$$\begin{aligned} M_D^{(0)}(\tau, \tau') = \int\int \mathrm{d}^2\Gamma_0 A(\Gamma_g(t_f - \tau; \Gamma_e(\tau'; \Gamma_0))) \\ \times \mathrm{e}^{\mathrm{i}(\omega_{eg} - U_{eg}(\Gamma_e(\tau'; \Gamma_0)))(\tau - \tau')} \rho_{gg}(\Gamma_0); \quad \tau \geq \tau'. \end{aligned} \tag{8}$$

According to equations (7, 8) the pump and dump pulses are decoupled. 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 equation (8) 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 and it 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) From equations (3, 7) the optimal pump pulse can be obtained which localizes phase space density at the intermediate target.

(iii) The optimized dump pulse projects the intermediate target to the ground state and localizes optimally the phase space density into the objective at a final time t_f.

The necessary condition for the existence of the connective pathway is that the function $A(\Gamma_g(t_f - t_d; \Gamma_e(t_d)))$ has nonvanishing contributions as it follows from equations (7) or (8). It should be pointed out that the outlined procedure can be in principle continued iteratively leading to fully optimized pump and dump fields.

3 Optimal control of the isomerization in Na_3F_2

The Na_3F_2 cluster has two ground state isomers separated by an isomerization barrier of 0.12 eV. The most stable isomer has C_s symmetry and consists of the Na_2F_2 ionic subunit with additional Na atom bound (*cf.* lower part of the right side of Fig. 1) and the second isomer has C_{2v} symmetry and contains one Na_3 metallic subunit bicapped with two F-atoms. The isomers are separated by a transition state (TS) whose structure is shown also in the lower part of the right side of Figure 1. Excited states of this system have been studied in the previous work [18] and it has been found that the first excited state arises primarily by the excitation of the single excess electron. In the first excited state which corresponds to the vertical excitation energy of 1.33 eV for the isomer I there is (i) one shallow local minimum related to the transition state separating both ground states isomer and (ii) global minimum which corresponds to a conical intersection between ground and first excited state (*cf.* right side of Fig. 1). It has been shown in the previous work [15] that isomerization through the conical intersection leaves the system with a high internal energy (~ 0.65 eV) which makes the population of the second isomer impossible by this process. Therefore, we apply our optimal control strategy described in Section 2. In the first step, the initial 50 K canonical ensemble in the Wigner representation was prepared corresponding to the ground state of C_s-Na_3F_2. In order to determine the intermediate target the ensemble was propagated classically for 300 fs on the first excited state and dumped back to the ground state every 25 fs

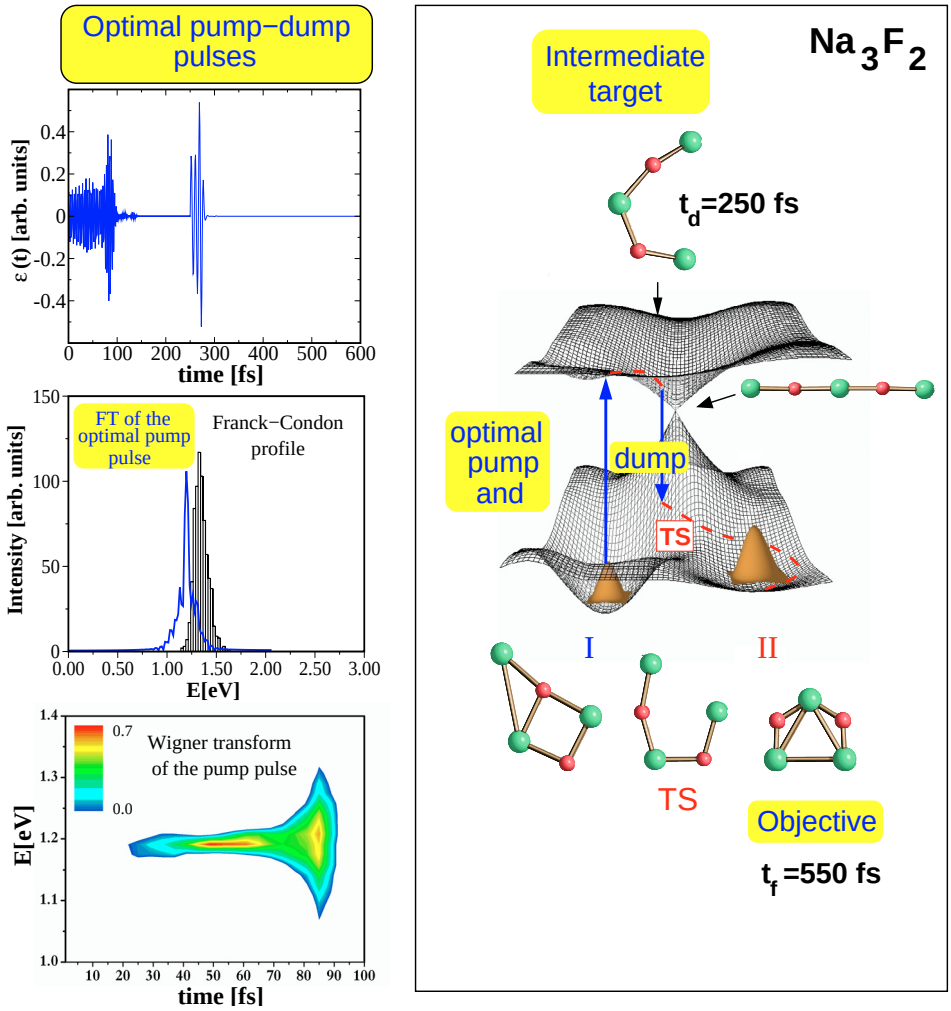

Fig. 1. Scheme for the pump-dump optimal control in Na_2F_3 cluster with geometries of the two ground state isomers and the transition state separating them, the conical intersection and the intermediate target are shown on the right hand side. The optimal electric fields corresponding to the pump and dump pulses are shown in the upper panel of the left side. The mean energy of the pump pulse is 1.20 eV and the mean energy of the dump pulse is 0.6 eV. 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 and Wigner transform of the optimal pump pulse are shown in middle and low panels of the left side, respectively.

and propagated in the ground state for 1 ps. The maximal residence time of at least 500 fs in the second isomer was obtained for the ensemble corresponding to the dump time of $t_d = 250$ fs (*cf.* right side of Fig. 1). This ensemble was used as an intermediate target and for the target operator in the Wigner representation we assumed the minimum uncertainty wave packet of the form

$$A(p_i, q_i) = \prod_{i=1}^{3N=15} \frac{1}{2\pi \Delta p_i \Delta q_i} \mathrm{e}^{-\frac{(q_i-\bar{q}_i)^2}{2(\Delta q_i)^2}} \mathrm{e}^{-\frac{(p_i-\bar{p}_i)^2}{2(\Delta p_i)^2}}, \qquad (9)$$

where $\bar{q}_i$ and $\bar{p}_i$ were obtained by averaging the ensemble coordinates and momenta at $t_d = 250$. The uncertainties in coordinates were defined such that they correspond to the spreading of the initial ensemble (≈0.053 Å). The analysis of the ensemble averaged momenta at $t_d = 250$ has shown that they are directed along the pathway which leads to the second isomer. The averaged kinetic energy corresponds to 75 percent of the isomerization barrier in the ground state which ensures that the ensemble remains localized in the basin corresponding to the second isomer. In order to calculate the pump pulse, the material response function $M(\tau, \tau')$ for the pump pulse equation (7) was calculated on a time grid of 1 fs, symmetrized and diagonalized using the standard Jacobi procedure. The largest eigenvalue obtained was 0.82 which corresponds to 82 percent efficiency of localizing the ensemble in the intermediate target. The optimal pump pulse has a complex temporal shape and consists of two portions with durations of ≈70 fs and ≈10 fs, respectively (*cf.* first pulse in the upper left panel of Fig. 1). Comparison of the Fourier transform of the pump pulse with the Franck-Condon profile for the C_s isomer (*cf.* middle left panel of Fig. 1) shows that the excitation of low lying vibrational modes is mainly responsible for reaching the intermediate target. This spectral region corresponds to the modes which involve

breaking of the Na-Na bond and opening of the C_s structure. Wigner transform of the optimal pump pulse shows that the first portion of the pulse is energetically very sharp and the second portion is much wider and symmetric with respect to the 1.2 eV reflecting the isotropic distribution of velocities in the initial ensemble. In order to obtain the dump pulse (*cf.* second pulse at $t_d = 250$ fs in the upper panel of left side of Fig. 1) which leads to the localization of the ensemble in the ground state objective, the intermediate target operator (9) was propagated on the ground state and dump pulse was determined by solution of the equations (4) and (8). The efficiency of the localization was 0.78 percent and obtained pulse has a duration of only ≈20 fs. The short duration of the dump pulse is consistent with the short time window for depopulation of the excited state since otherwise the system would gain very rapidly a large amount of excess energy on the excited state.

4 Conclusion

A new strategy for optimal pump-dump control in multidimensional system was developed by introducing the concept of intermediate target in the excited state. The role of the intermediate target is to select the appropriate Franck-Condon window at a given time delay between the pump and dump pulses which is mandatory for reaching the objective and which ensures the existence of the connective pathway between initial state and the objective in the ground state. The scope of the concept was shown on the example of Na_3F_2 cluster by optimizing the pump and dump pulses which drive the isomerization process in Na_3F_2 *via* optimal pathway and suppress the radiationless transition through the conical intersection. The analysis of the pulse shapes allows to identify the processes which are responsible for the obtained pulse shapes and serve as a guidance for gaining better understanding of experimentally shaped pulses.

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References

1. B. Kohler, V.V. Yakovlev, J. Che, J.L. Krause, M. Messina, K.R. Wilson, N. Schwentner, R.M. Whitnell, Y.J. Yan, Phys. Rev. Lett. **74**, 3360 (1995)
2. N.F. Scherer, A.J. Ruggiero, M. Du, G.R. Fleming, J. Chem. Phys. **93**, 856 (1990)
3. A.M. Weiner, D.E. Leaird, G.P. Wiederrecht, K.A. Nelson, Science **247**, 1317 (1990)
4. A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, G. Gerber, Science **282**, 919 (1998)
5. S. Vajda. A. Bartelt, E.C. Kaposta, T. Leisner, C. Lupulescu, S. Minemoto, P. Rosendo-Francisco, L. Wöste, Chem. Phys. **267**, 231 (2001)
6. S.A. Rice, S.P. Shah, Phys. Chem. Chem. Phys. **4**, 1683 (2002)
7. R.J. Levis, H.A. Rabitz, J. Phys. Chem. A **106**, 6427 (2002)
8. S.A. Rice, Science **258**, 412 (1992)
9. D.J. Tannor, S.A. Rice, J. Chem. Phys. **83**, 5013 (1985)
10. D.J. Tannor, R. Kosloff, S.A. Rice, J. Chem. Phys. **85**, 5805 (1986)
11. R. Kosloff, S.A. Rice, P. Gaspard, S. Tersigni, D.J. Tannor, Chem. Phys. **139**, 201 (1989)
12. Y. Yan, J. Che, J. Krause, Chem. Phys. **217**, 297 (1997)
13. M. Hartmann, J. Pittner, V. Bonačić-Koutecký, A. Heidenreich, J. Jortner, J. Chem. Phys. **108**, 3096 (1998); R. Mitrić, M. Hartmann, B. Stanca, V. Bonačić-Koutecký, P. Fantucci, J. Phys. Chem. **105**, 8892 (2001)
14. M. Hartmann, J. Pittner, V. Bonačić-Koutecký, J. Chem. Phys. **114**, 2106 (2001)
15. M. Hartmann, J. Pittner, V. Bonačić-Koutecký, J. Chem. Phys. **114**, 2123 (2001)
16. Y. Yan, R.E. Gillilan, R.M. Whitnell, K.R. Wilson, J. Phys. Chem. **93**, 2320 (1993)
17. B. Kohler, J.L. Krause, F. Raksi, C. Rose-Petruck, R.M. Whitnell, K.R. Wilson, V.V. Yakovlev, Y. Yan, J. Phys. Chem. **97**, 12602 (1993)
18. V. Bonačić-Koutecký, J. Pittner, J. Koutecký, Chem. Phys. **210**, 313 (1996)