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The "Hydrogen-Subway"—A Tunneling Approach to Intramolecular Hydrogen Transfer Reactions Controlled by Ultrashort Laser Pulses

N. Došlić,[†,‡] O. Kühn,[†] J. Manz,[†] and K. Sundermann*[,†]

Institut für Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustr. 3, D -14195 Berlin, Germany, and Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

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Isomerization reactions from a reactant state to a near-degenerate product state which are typical for intramolecular hydrogen transfer may be achieved by means of ultrashort picosecond or sub-picosecond laser pulses having three consecutive time domains. Initially, the laser field is switched on such that the wave packet representing the reactant is converted into a superposition of near-degenerate delocalized states of the "dressed" molecule, with level spacing ΔE^{ϵ}. In the second stage, the laser field ϵ is kept approximately constant until the wave packet has tunneled from the reactant to the product configuration, during the tunneling time $\tau^{\epsilon} = h/2\Delta E^{\epsilon}$. Finally the field is switched off in such a way that the wave packet is stabilized as the target product state. This approach is suggested by optimal control theory and applied to a one-dimensional model resembling substituted malonaldehydes. Here it is found that the laser-driven tunneling requires time-integrated laser field intensities fifty times smaller than the alternative pump−dump approach which drives the reactant wave packet over the potential barrier toward the product state without tunneling. Various applications and extensions of this method are discussed.

1. Introduction

The purpose of this paper is to present a new method for the control of isomerization reactions, in particular intramolecular hydrogen transfer, by means of ultrashort laser pulses, in the picosecond or sub-picosecond time domain. Different strategies for laser-driven isomerization have been suggested in the literature. They have in common that the overall reaction is achieved by a transfer of the initial wave packet from the reactant configuration *over* the potential barrier which separates the reactants from the products, toward the product configuration. First, a pump−dump scheme has been proposed which uses infrared (IR) picosecond or sub-picosecond laser pulses designed "by hand"[1,2] or by means of optimal control theory.[3] The transfer proceeds on a single potential energy curve which usually corresponds to the electronic ground state. Second, the pump−dump scheme has been studied for a transfer involving electronic excited states and therefore requiring laser pulses in the visible or ultraviolet (UV) domains.[4,5] This strategy is similar to the original pump−dump approach to controlling photodissociation as suggested by Tannor and Rice.[6,7] The studies in refs 3 and 5 are based on the general control theory as developed by Rabitz and co-workers.[8,9] In all of these methods, the required laser fields are usually quite strong, with maximum intensities typically in the domains of TW/cm^2 in order to achieve ≈90% product yields. These high intensities may cause a problem since they may be close to the so-called Keldysh limit[10] where ionization starts to compete with laser control, i.e., the system to be controlled is destroyed. (For a discussion, see, for example, ref 11.)

The present alternative scheme for ultrafast laser control of isomerization reactions differs from the previous approaches since it requires laser intensities which are considerably smaller than in the pump−dump method and, therefore, shall be well below the Keldysh limit. This goal is achieved following a completely different strategy in which the wave packet is not driven over but *through* the barrier. Below we shall demonstrate that this laser-driven tunneling through the potential barrier separating different isomers can be achieved most easily for hydrogen transfer reactions; hence, our approach shall be called the "hydrogen-subway".

In the tunneling regime, the double well potential characteristic for isomerization reactions can often be reduced to the lowest tunneling doublet. The laser-driven dynamics in this effective two-level system has been investigated in great detail in the isolated case as well as under the influence of a linearly coupled heat bath. (For a recent, review see ref 13.) Here, particular emphasis has been put on the coherent destruction of tunneling by means of monochromatic continuous-wave electromagnetic fields. Coherent destruction of tunneling implies that an initial localized state in a symmetric two-level system stays localized even though it is not an eigenstate of the molecular Hamiltonian.[14] The modification of this effect upon coupling to a dissipative environment has been investigated, e.g., by Makri and co-workers for the symmetric[15] and the asymmetric[16] two-level system. The opposite case, namely the localization of an initially delocalized state of an isolated symmetric two-level system by means of semi-infinite laser pulses has been studied by Metiu and co-workers.[17] The inclusion of vibrationally excited states in the reactant and product potential wells and the CW laser control of their populations was considered by Cukier et al.[18] Other recent applications of laser-driven molecular systems include, e.g., the control of harmonic generation in H_2^{+}[19] and the demonstration of field-induced transparency of a periodically oscillating potential barrier.[20]

Our new method for laser-driven isomerization dynamics in asymmetric double minimum potentials is demonstrated here

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* Author to whom correspondence should be addressed.

[†] Freie Universität Berlin.

[‡] Ruđer Bošković Institute.

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for a one-dimensional (1D) model with parameters tailored to hydrogen transfer in substituted malonaldehydes.[12] The model is presented in Section 2. For reference we use this model first in order to simulate laser-driven isomerization by means of the traditional above barrier pump–dump strategy employing the optimal control method,[3,5,8] see Section 3. Then, in Section 4, we shall again use optimal control theory, but now with a rather tough constraint on the time-integrated laser intensities. The resulting optimal laser fields will turn out to be entirely different from those of the previous results, and they will serve to discover the "hydrogen-subway" mechanism. A clear, illuminating example of our approach will also be discussed in Section 4. In Section 5, we comment on various applications and extensions.

2. Model and Techniques

To simulate the laser-driven isomerization, we propagate representative wave packets, $\psi(t)$, from the initial reactant (R) to the different final product (P) configuration, subject to a laser field $\epsilon(t)$. For clarity of presentation we employ a model which is based on rather simple assumptions. Hence we shall assume that the molecule is in its electronic ground state, we neglect the effect of rotations, and suppose that the laser field is polarized along the dominant molecular dipole component μ. In the semiclassical dipole approximation, the time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi}{\partial t} = H_{\mathrm{mol}}\psi - \mu\epsilon(t)\psi \tag{1}$$

Moreover, we suppose that the reaction proceeds along a Cartesian reaction coordinate q, with effective mass m, and we neglect any coupling to environmental degrees of freedom. The corresponding one-dimensional molecular Hamiltonian is

$$H_{\mathrm{mol}} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + V(q) \tag{2}$$

The potential $V(q)$ has two nonequivalent minima at $q = \pm q_0$ representing the domain of reactants ($q < 0$) and products ($q > 0$) separated by the barrier having its maximum, $V^{\ddagger}$, at or close to $q = 0$. The mass entering here is taken as the hydrogen mass, i.e., $m = m_{\mathrm{H}}$.

The corresponding time-independent Schrödinger equation

$$H_{\mathrm{mol}}\phi_n = E_n\phi_n \tag{3}$$

yields the eigenstates ϕ_n and eigenenergies E_n of the free molecule. They may be classified as reactant or product states if they are localized preferably in the reactant and product configurations and have energies E_n well below the top of the potential barrier $V^{\ddagger}$. On the other hand, there are delocalized transition states with energies just below or above the barrier $V^{\ddagger}$. We shall assume that the barrier is rather low and the asymmetry, Δ, of the potential is rather weak so that $V(q)$ supports only one reactant state $\phi_0 = \psi_{\mathrm{R}}$ and one near-degenerate product state $\phi_1 = \psi_{\mathrm{P}}$, together with delocalized transition states ϕ_n , $n = 2, 3, \cdots$

As a specific example, we consider the potential energy function

$$V(q) = \frac{\Delta}{2q_0}(q - q_0) + \frac{V^{\ddagger} - \Delta/2}{q_0^{\,4}}(q - q_0)^2(q + q_0)^2 \tag{4}$$

shown in Figure 1. The parameters are adapted from ref 12 and are tailored to nonsymmetric substituted malonaldehydes (see figure caption.). For the dipole function we assume a linear dependence on the hydrogen transfer coordinate, i.e., $\mu(q) = \mu' q$. For simplicity we use $\mu' = e$ even though the amount of charge transferred in malonaldehydes is likely to be less than e. This should be kept in mind when estimating the field strengths in applications to specific molecules.

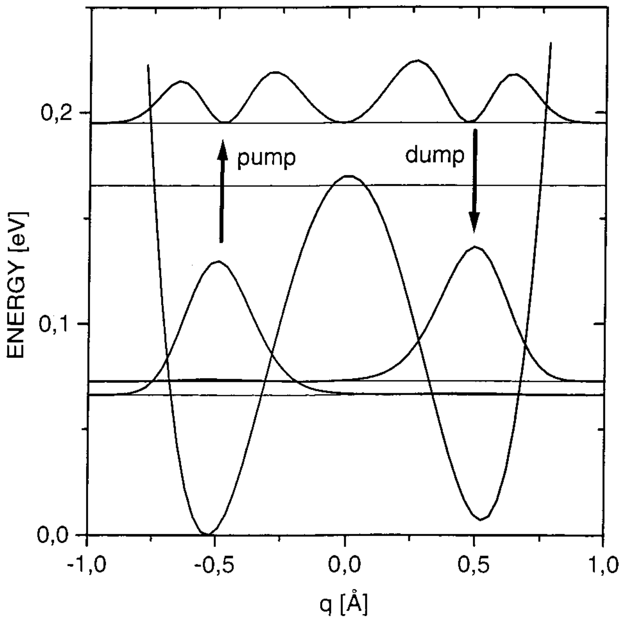

Figure 1. Hydrogen transfer from the reactant state ψ_{R} (left) via a transition state $\psi^{\ddagger}$ above the potential barrier to the product state ψ_{P} (right), induced by two subsequent (pump and dump) infrared picosecond laser pulses. The model potential energy along the reactant coordinate, representing substituted malonaldehyde (adapted from ref 12) is shown together with the energies E_{i} and the densities $\rho_{\mathrm{i}} = |\phi_{\mathrm{i}}|^2$ of the lowest eigenstates ϕ_0, ϕ_1, ϕ_2, ϕ_3 where $\phi_0 = \psi_{\mathrm{R}}$, $\phi_3 = \psi^{\ddagger}$, and $\phi_1 = \psi_{\mathrm{P}}$. The potential parameters are as follows: barrier height $V^{\ddagger} = 0.00625E_{\mathrm{h}}$, potential minima at $q = \pm q_0$, $q_0 = 1a_0$, and asymmetry $\Delta = 0.000257E_{\mathrm{h}}$.

A large class of molecules exhibiting hydrogen transfer between near-degenerate reactant and product states has been surveyed recently by Perrin and co-workers.[21] All of those molecules are designed to have rather small barriers and rather weak asymmetries induced by slightly different substitutions, e.g., by isotopic labeling of two equivalent sites of an overall symmetric molecular scaffold.

The preparation of the time-dependent wave packet starts from the reactant state, $\psi(t = 0) = \psi_{\mathrm{R}}$ and the electric field $\epsilon(t)$ is designed such that $\psi(t)$ should approach the product state $\psi_1 = \psi_{\mathrm{P}}$ at the end of the laser pulse, $\psi(t) \rightarrow \psi_{\mathrm{P}}$ for $t = t_{\mathrm{p}}$. For this purpose we shall employ different choices of $\epsilon(t)$ which lead to entirely different mechanisms for the laser-driven isomerization, in Sections 3 and 4. Some of the electric fields $\epsilon(t)$ shall be given in analytical forms, whereas the others shall be designed by means of optimal control theory as put forward by Rabitz and collegues[8,9] (See, also[5,22]). In the latter case, $\epsilon(t)$ is obtained by maximizing the functional

$$F = \langle|\psi(t_{\mathrm{p}})|\psi_{\mathrm{P}}\rangle|^2 - \alpha\int_0^{t_{\mathrm{p}}} \mathrm{d}t\frac{\epsilon^2(t)}{S(t)} - 2\mathrm{Re}\Big[\langle\psi_{\mathrm{i}}(t_{\mathrm{p}})|\psi_{\mathrm{P}}\rangle\int_0^{t_{\mathrm{p}}} \mathrm{d}t \\ \Big\langle\bar{\psi}(t)\Big|\frac{\partial}{\partial t} + i[H_{\mathrm{mol}} - \mu\epsilon(t)]\Big|\psi(t)\Big\rangle\Big] \tag{5}$$

The first term describes the overlap of the laser-driven wave function $\psi(t_{\mathrm{p}})$ with the target state ϕ_{f}, the second is the time-integrated laser intensity, within the pulse duration t_p of the laser pulse, weighted by the inverse shape function $S(t)^{22}$ and the penalty factor α. In the subsequent application we use a plateau-type shape function with 1/6 of the overall time reserved for some $\sin^2$ -type switch on and off behavior. The third term imposes the constraint that the resulting wave function $\psi(t)$ should obey the time-dependent Schrödinger eq 1. The function $\bar{\psi}(t)$ in eq 5 is a Lagrange multiplier. Iterative solution of the problem $\delta F = 0$ in practice leads to a local maximum depending on the initial guess $\tilde{\epsilon}(t)$ for $\epsilon(t)$. The numerical solution of the time-dependent Schrödinger eq 1 which is required in the optimization procedure is done in coordinate space, $\psi(q, t) = \langle q|\psi(t)\rangle$ by means of the Fast Fourier Transform technique.[23] The corresponding time-dependent populations of the molecular states, ϕ_n, are then calculated from $P_n(t) = |\langle\phi_n|\psi(t)\rangle|^2$.

3. Laser-Induced Hydrogen Transfer above the Potential Barrier

First let us consider the traditional approach of Paramonov et al.[1,2] which drives the hydrogen transfer reaction over the potential barrier. This will serve as a reference in the following. As indicated in Figure 1 one employs a series of two IR laser pulses, $\epsilon(t) = \epsilon_1(t) + \epsilon_2(t - t_d)$ with delay time t_d. Each of the two pulses has the form

$$\epsilon_i(t) = \epsilon_{0i} \cos(\omega_{0i}t) \sin^2 (t\pi/t_{p_i}) \qquad 0 \le t \le t_p \qquad (6)$$

with amplitudes ϵ_{0i}, carrier frequencies ω_i, $\sin^2$-shape and pulse duration t_{p_i}. The overall duration is thus $t_p = t_{p2} + t_d$. The first pump—pulse induces the transition from the initial reactant state ϕ_0 to the delocalized state ϕ_3 above the potential barrier, and the second pulse dumps the wave packet into the product state ϕ_1. This pump—dump scheme is illustrated schematically by vertical arrows in Figure 1. Using laser pulses with parameters $\epsilon_{01} = 0.86 \times 10^{-3}$ E_h/ea_0, $\omega_{01} = 1038$ cm^{-1}, and $t_{p1} = 1100$ fs, and $\epsilon_{02} = 0.915 \times 10^{-3}$ E_h/ea_0, $\omega_{02} = 990$ cm^{-1}, $t_{p2} = 1200$ fs, the overall product yield reached after the pulses are over is $P_1(t_p) = 0.95$ (not shown). This is the maximum yield that we could achieve within the overall pulse duration, $t_p = 2.0$ ps, by means of two IR picosecond laser pulses with $\sin^2$-shape.

As an alternative approach to laser-induced hydrogen transfer, let us consider next the results obtainable for the same system by means of optimal control theory.[8,9] For this purpose, we shall use two different realizations of the general approach outlined in Section 2 (see eq 4). In the first case, we search for the local maximum of the functional F, starting from the previous series of two pump—dump laser pulses with $\sin^2$-shape as the "educated guess", $\tilde{\epsilon}(t)$, and allowing for high laser intensity by choosing a small penalty factor $\alpha = 25$ in eq 5. The resulting optimal laser field and population dynamics is shown in Figure 2. As may have been anticipated, these results resemble closely the two-pulse pump—dump scheme discussed before. In particular, the population dynamics confirms the pump—dump mechanism of laser-induced hydrogen transfer above the barrier. However, there is an improved overall product selectivity, $P_1(t_p) = 0.99$, which has been achieved by means of the optimal field $\epsilon(t)$ at the expense of a deviation from the analytical guess $\tilde{\epsilon}(t)$ (eq 6).

4. The "Hydrogen-Subway"

As our next approach to laser-induced hydrogen transfer, we shall again use optimal control theory but now with a tough constraint on the time-integrated intensity. We increase the penalty factor to $\alpha = 400$ in eq 5 in order to reduce the maximum field strength and, therefore, to avoid competing ionization processes. Moreover, we impose another constraint by reducing the pulse duration t_p to 1.5 ps. As an inital guess we choose a constant electric field $\tilde{\epsilon}(t) = 10^{-3}$ E_h/ea_0 which corresponds approximately to the largest field amplitude of the optimized pump—dump pulse in Figure 2. The resulting new optimal field $\epsilon(t)$ is shown in Figure 3, together with the population dynamics of the molecular eigenstates. Obviously, these results are entirely different from those shown in Figure 2. They suggest a new mechanism of laser-pulse-driven hydrogen transfer. Most importantly, the population dynamics shows dominant population exclusively for the reactant (ϕ_0) and product (ϕ_1) states, with just marginal contributions from any other delocalized state ϕ_n, $n \ge 2$, close to or above the barrier (not shown). This implies that the hydrogen atom is no longer driven above, but through the barrier—the traditional pump—dump approach has been replaced by the "hydrogen-subway"! By construction the optimal field is much weaker for the "hydrogen-subway" than for the pump—dump mechanism, yet it achieves about the same product yield, i.e., $P_1(t_p) = 0.99$ (compare Figures 2 and 3).

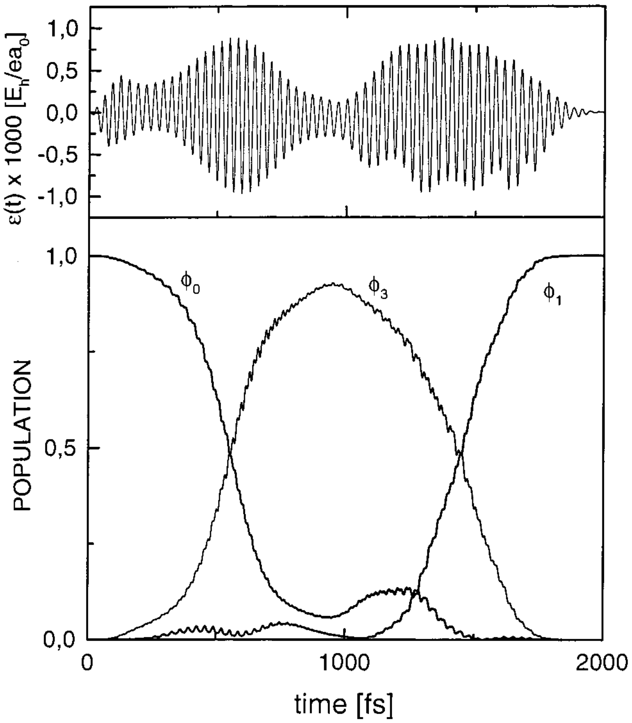

Figure 2. Electric field (top) and population dynamics (bottom) for optimal control of hydrogen transfer in the model system of Figure 1. The optimization has been achieved by means of the iterative technique of refs. 5 and 8 starting from the analytical field, eq 6, and using a small penalty factor $\alpha = 25$. The marginal populations of the other states are not shown.

To understand, interpret, and eventually even exploit the "hydrogen-subway" mechanism, let us analyze the optimal field $\epsilon(t)$ shown in Figure 3 in detail. Apparently, we may distinguish three subsequent stages: (1) the initial period ($0 \le t \le t_i \approx 0.15$ ps where the field is switched on, (2) an intermediate period ($t_i \le t \le t_f \approx 1.25$ ps where the field is approximately constant, and (3) the final period ($t_f \le t \le t_p$) where the field is switched off. The corresponding population dynamics indicates marginal variations during the initial and final period of switch on/off, and tunneling during the intermediate period with (approxi-

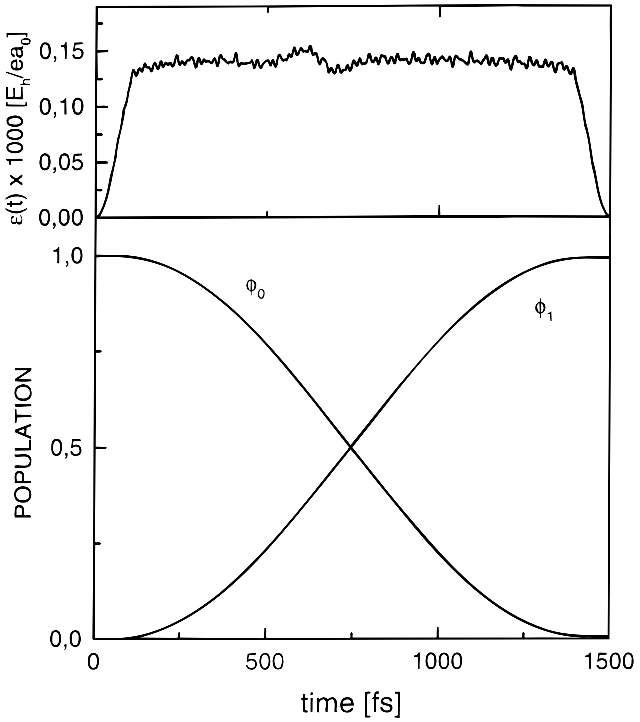

Figure 3. Same as Figure 2, but with a tough constraint on the time-integrated intensity ($\alpha = 400$). Further, the pulse duration was chosen as 1.5 ps. The iteration procedure was initialized with a constant field, $\tilde{\epsilon} = 10^{-3}$ E_h/ea$_0$.

mately) constant field strength. Those empirical observations suggest the following mechanism behind the "hydrogen-subway":

(1) Initially, the field is switched on such that the wave packet representing the reactant, $\psi(t = 0) = \phi_0$, is converted into a superposition of two near-degenerate delocalized states

$$\psi(t_i) = \frac{1}{\sqrt{2}}(\phi_0^\epsilon + \phi_1^\epsilon)e^{i\eta_i} \tag{7}$$

with irrelevant phase η_i. The delocalized states ϕ_0^ϵ and ϕ_1^ϵ are obtained as eigenfunctions of the molecule "dressed" by the static field ϵ which is maintained during the intermediate period, thus

$$(H_{\mathrm{mol}} - \mu\epsilon)\phi_i^\epsilon = E_i^\epsilon\, \phi_i^\epsilon \tag{8}$$

(2) In the intermediate stage, $t_i \le t \le t_f$, where $\epsilon \approx$ constant, the wave packet is converted from $\psi(t_i)$ to

$$\psi(t_f) = \frac{1}{\sqrt{2}}(\phi_0^\epsilon - \phi_1^\epsilon)e^{i\eta_f} \tag{9}$$

again with irrelevant phase. Since ϕ_0^ϵ and ϕ_1^ϵ are both delocalized, the conversion from $\psi(t_i)$ to $\psi(t_f)$ implies tunneling from the initial to the final wave packets which are localized in the reactant and product configurations, respectively. The corresponding tunneling time is obtained from the relation

$$\tau^\epsilon = \frac{1}{2}h/\Delta E^\epsilon \tag{10}$$

with the energy gap $\Delta E^\epsilon = E_1^\epsilon - E_0^\epsilon$. (3) In the final stage the field is switched off, and the wave function is stabilized as the product target state

$$\psi(t_p) \approx \phi_1 e^{i\eta_{tp}} \tag{11}$$

In order to test this mechanism we design an analytical laser field which corresponds directly to the three stages:

$$\begin{aligned} \epsilon(t) &= \epsilon\,\sin^2(t\pi/2t_i) && 0 \le t \le t_i \\ \epsilon(t) &= \epsilon = \text{constant} && t_i \le t \le t_f \\ \epsilon(t) &= \epsilon\,\sin^2[(t_p - t)\pi/2(t_p - t_f)] && t_f \le t \le t_p \end{aligned} \tag{12}$$

The parameters ϵ, t_i, t_f in eq 13 may be optimized in order to achieve maximum product yields. In practice this optimization may be carried out starting from an educated guess obtained as follows: The optimum field strength should be close to the initial guess $\tilde{\epsilon}$ which is chosen to yield perfectly delocalized states $\phi_0^{\tilde{\epsilon}}$ and $\phi_1^{\tilde{\epsilon}}$. For the model potential given in eq 4 and the linear dipole functions, this field should compensate the asymmetry term $(q - q_0)\Delta/2q_0$. The duration of the tunneling domain should be close to the tunneling time $t_f - t_i \approx \tau^{\tilde{\epsilon}}$.

The resulting electric field which has been optimized "by hand" is shown in Figure 4 together with the population dynamics. The optimal field strength $\epsilon = 0.137 \times 10^{-3}$ E_h/ea_0 is close to the value $\tilde{\epsilon} = 0.129 \times 10^{-3}$ E_h/ea_0 which yields perfectly delocalized states $\phi_0^{\tilde{\epsilon}}$ and $\phi_1^{\tilde{\epsilon}}$. The slight deviation can be shown to result in part from the nonperfect localization of the initial and final states as will be discussed in a subsequent publication. The length of the tunneling period for the optimized field is $\tau^\epsilon = 1.25$ ps which is of course shorter than the guess $\tau^{\tilde{\epsilon}} = 1.43$ ps due to finite switch on and switch off times and the slightly different optimized field strength.

The corresponding transitions of the wave packet

$$\begin{aligned} \psi(0) = \phi_0 \rightarrow \psi(t_i) = \frac{1}{\sqrt{2}}(\phi_0^\epsilon + \phi_1^\epsilon)e^{i\eta_i} \rightarrow \psi(t_f) \\ = \frac{1}{\sqrt{2}}(\phi_0^\epsilon - \phi_1^\epsilon)e^{i\eta_i} \rightarrow \psi(t_p) \approx \phi_1 \end{aligned} \tag{13}$$

is illustrated by snapshots of the corresponding densities, $\rho = |\psi|^2$, in Figure 5, confirming the three steps (switch on − tunnel −switch off) of the laser-driven "hydrogen-subway".

5. Conclusions

The present alternative approach to laser control of isomerization reactions, i.e., laser-pulse-induced tunneling, has been demonstrated here by means of simulations for a simple model of intramolecular hydrogen transfer in an asymmetric double well potential. The parameters have been tailored to resemble the situation in nonsymmetric derivatives of malonaldehyde (adapted from ref 12, see also ref 21). Our model simulations highlight substantial advantages of this "hydrogen-subway" mechanism, in comparison with previous approaches.[1,2,4] Moreover, they point to several conditions that should be fulfilled in order to verify the mechanism in hydrogen transfer or in other systems, and they should serve as a basis for various applications and extensions. In particular, we would like to emphasize the following points.

The most important advantage of the "hydrogen-subway" mechanism is the reduction of the (time-integrated) laser intensity which is required for driving the isomerization from the reactants to the products in comparison with traditional approaches. In the present case, for example, the pump−dump approach of refs 1 and 2 requires the maximum intensity of $I_{\max} = 590$ GW/cm^2 to induce the isomerization by two IR laser

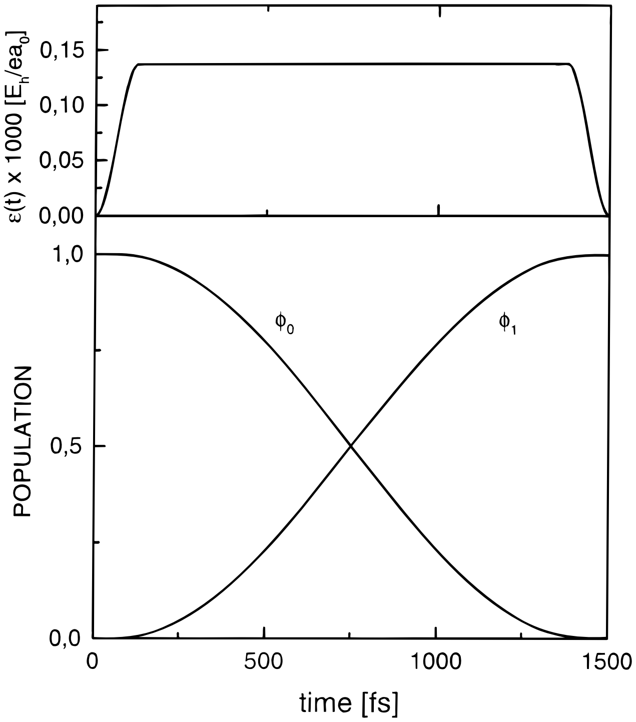

Figure 4. Model demonstration of the “hydrogen-subway” using the analytical pulse shape of eq 12 (for parameters, see text).

pulses, with overall pulse duration $t_p = 2.0$ ps, via the “detour” to a delocalized transition state above the potential barrier. In contrast, the “hydrogen-subway” requires only $I_{max} = 11.6$ GW/cm^2 for laser-induced tunneling through the barrier. As a consequence, our mechanism shall more easily avoid competing processes involving electronic transitions and in particular ionization which results in a destruction of the system beyond the Keldysh limit.

Another advantage is the suggested time scale which is in the domain of about 1 ps and, therefore, more suitable to modern techniques of pulse shaping.[24,25] In contrast, for example the pump−dump approach of ref 4 calls for UV or visible laser pulses in the domain of ca. 10−20 fs, i.e., much shorter than the time scale of hydrogen transfer in the excited electronic state which is induced and stopped by the consecutive pump- and dump-pulses, and therefore, not so easily accessible to present laser pulse shaping technology.

The third advantage one can deduce from comparison of Figures 3 and 4, which have been derived using optimal control theory[5,8,9] and the simple “hand-made” didactic example, respectively, is the apparent robustness of the present approach: We have achieved close to 100% selectivity irrespective of the exact shape of the laser pulse, provided the overall sequence included the three subsequent stages: switch on, tunneling, and switch off. This shall in practice allow for a wide range of laser pulse shapes. An extreme limit would be a half-cycled pulse where the time reserved for tunneling approaches zero. The generation of high-power half-cycled pulses in the subpicosecond domain has been demonstrated by Bucksbaum and co-workers.[26] We have tested such half-cycled pulses and found that one can achieve a 90% isomerization yield using a single pulse of the form of eq 6 with $\epsilon_0 = 1.5 \times 10^{-3}$ E_h/ea_0, $t_p = 2.3$ ps, and $\omega_0 = 0$. Therefore, the somewhat idealized didactic example shown in Figure 3 presents the most efficient realization of *ultrafast* hydrogen switching.

Favorable conditions for the “hydrogen-subway” include tunneling times, τ^ϵ, which should be in the range of about 1 ps or below, in order to avoid competing dissipative processes, e.g., due to intramolecular vibrational redistribution (IVR). This imposes the condition that the level spacing ΔE^ϵ of the dressed molecule during the tunneling period should be in the range $\Delta E^\epsilon > 30$ cm^{-1}. This condition should be fulfilled most easily for hydrogen transfer; hence, the mechanism has been called the “hydrogen-subway”. Other isomerizations which involve the rearrangement of heavier nuclei usually have smaller splittings between delocalized states, $\Delta E^\epsilon << 10$ cm^{-1}. This implies all-too-long tunneling times $\tau^\epsilon >> 10$ ps which are not suitable since competing processes which destroy the phase relationships of the wave function, e.g., collisions with solvent molecules, become dominant.

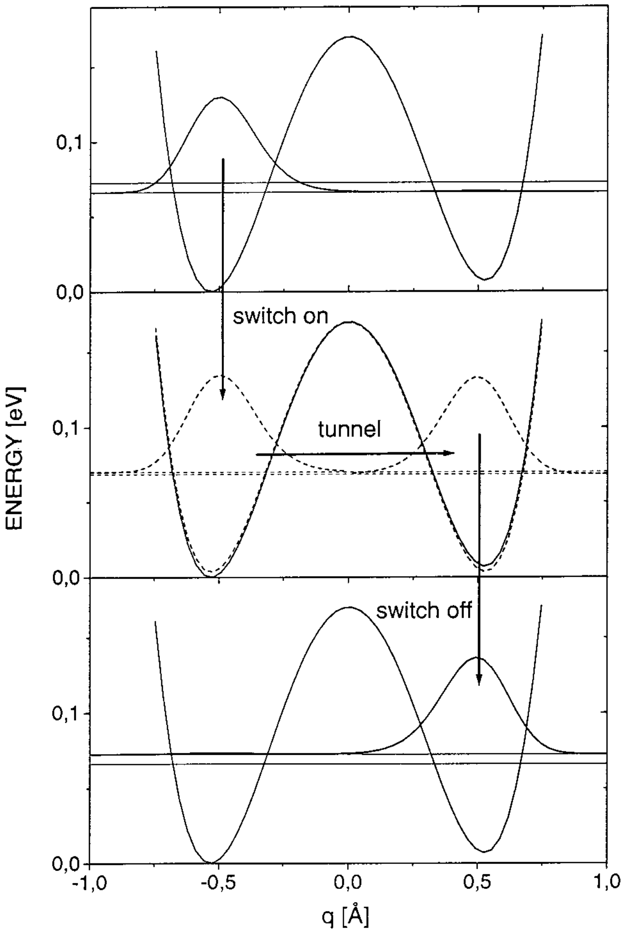

Figure 5. The “hydrogen-subway” demonstrated by a series of snapshots which illustrate the wave packet dynamics corresponding to the time evolution in the electric field and the populations shown in Figure 4. The snapshots are taken at times $t = 0$ (top panel), $t = t_i = 0.125$ ps, $t_f = 1.375$ ps (middle panel, left and right densities before and after tunneling), and $t = t_p = 1.5$ ps (bottom panel). In the middle panel, the potential of the free molecule (solid line) is compared with the effective potential $V - \mu\epsilon$ of the dressed molecule (dashed line) during the tunneling period, $t_i \leq t \leq t_f$. Also given is the tunneling doublet for the dressed molecule which has a splitting of ΔE^ϵ.

In the present case, the hydrogen transfer has been demonstrated for a model system with a rather low potential barrier implying only one local reactant plus one product state with energies below the potential barrier. The new mechanism for laser control is, however, not restricted to systems with small potential barriers. It may also be used, for example, to induce tunneling between near-degenerate vibrationally excited reactant and product states in asymmetric systems with higher barriers. This requires laser fields strong enough to transform those states into a pair of near-degenerate delocalized states with level splitting ΔE^ϵ which is suitable for tunneling. Therefore the general strategy which can be derived from the present results contains the laser-induced tunneling in a delocalized two-level system of the dressed molecule. The localized superpositions of the delocalized states can be created from any suitably localized initial and final states of the free molecule during the switch on and switch off periods, respectively. This laser control of transitions from reactant to near-degenerate but different product states should be distinguished from complementary laser control schemes for near-degenerate pairs of symmetric molecules, e.g., suppression[14] or acceleration of tunneling,[27] or localization of pairs of delocalized states in symmetric systems.[17]

There are many possible applications and extensions of the present laser control scheme. On the methodological side, we shall investigate the effects of several assumptions which have been made for the present simple one-dimensional model. In particular, this includes the competing effects of additional degrees of freedom.[28] Moreover we should explore various possible combinations of the present approach with previous ones. For instance, one may employ series of IR picosecond laser pulses[1,2] to excite the reactants to a selected vibrationally excited state which has a near-degenerate product state, serving as a pair of two localized states which are suitable to start the "hydrogen-subway".[28] Moreover one could combine the present approach with that of Holthaus[27] to reduce the tunneling time. This would be advantageous in order to beat competing processes such as IVR. Further, such an approach could be used even to drive tunneling of heavier nuclei in asymmetric molecules. Various applications could include laser-induced preparations of specific tautomers or isotopomers (e.g., selective induction of H- but not D−transfer), selective desorption of specific isotopomers from surfaces (e.g., NH_3 but not ND_3 from Cu; see, for example, ref 29), and selective acceleration of forward reactions versus suppression of back reactions by means of nonsymmetric switch on and switch off parts of the overall laser pulse. Work along those lines is in progress.

6. Epilogue

Finally, we would like to comment on the use of optimal control theory which has been employed in order to discover the present alternative mechanism of laser-controlled intramolecular hydrogen transfer. In a wise, concluding remark summarizing the information theoretical approach to chemical reaction dynamics and the road ahead, R. D. Levine[30] has advocated that, in principle, all possible reaction paths should be considered without any bias except for dynamical constraints and conservation laws. On this basis, one might discover the most efficient pathways to reactivity, but "life will always be full of surprises".[30] The remaining problem thus is: How can one be sure that we really consider all possible ways from the reactants to the products? In the present case, we have to admit that we did not see the "hydrogen-subway" scheme, a priori, because we had been biased by the traditional pump−dump approach. We saw it only a posteriori, i.e., after recognizing and analyzing the results of optimal control theory. In the context of Levine's information theoretical approach, it is challenging to evaluate the surprisal of this laser-driven reaction mechanism.

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