Selective Excitation of Vibrational States by Shaping of Light-Induced Potentials

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In this Letter we describe a method for population transfer using intense, ultrafast laser pulses. The selectivity is accomplished by careful shaping of light-induced potentials (LIPs). Creation and control of the LIPs is accomplished by choosing pairs of pulses with proper frequency detunings and time delays. As an example, selective population transfer is demonstrated for a three-state model of the sodium dimer.

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Excitation of molecules with intense, ultrafast laser pulses has led to the discovery of a number of exotic and unexpected effects [1–6]. In the strong response regime, an adiabatic representation is often an appropriate description of the dynamics. This representation has been used to understand such processes as bond softening [1,3] and stabilization [7]. The dynamics of these systems can be explained in a dressed state picture by analyzing wave packet motion on light-induced potentials (LIPs).

The concept of LIPs has been used previously to predict the existence of bound states trapped in light-induced adiabatic wells [1]. These states were subsequently observed experimentally via photoelectron [2] and photodissociation [6] spectroscopy. Time gating of light-induced avoided crossings has been proposed as a method for performing vibrational population inversion [1]. The idea is to drive a wave packet to a desired final state by using precisely controlled femtosecond pulses to selectively open and close field-induced avoided crossings. A potential shortcoming of this method is a possible loss of selectivity due to the large bandwidth of the excitation pulse, which excites a superposition of many vibrational states.

In this Letter we analyze a method to achieve selective population transfer from a single vibrational level on a ground electronic state to a single vibrational level on an excited electronic state. The method uses intense, ultrafast laser pulses to create and shape light-induced potentials. The selectivity of the method is guaranteed by the use of picosecond pulses and adiabatic deformation of the light-induced potentials. We show that temporal and spatial adiabaticity *together* are required to achieve efficient population transfer while conserving the vibrational number of the initial state on the final state.

The main difference between the method described here and the time-gating method proposed previously [1] is that we make full use of the adiabatic shaping of the LIP responsible for population dynamics, while the time-gating method concentrates on the precise timing of the opening and closing of avoided crossings. In addition to the possibility of attaining selective population transfer, there are a number of potential experimental advantages of the method proposed here. First, in the present scheme it is beneficial, but not crucial, to exploit the presence of a two-photon resonance. Second, there is no upper bound on the intensity of the laser fields (aside from the competition of additional mechanisms such as ionization and multiphoton processes). In the time-gating method, the Rabi frequency cannot be larger than the vibrational spacing [1].

We show below that a recently proposed method for adiabatic passage via light-induced potentials (APLIP) [8] is one special case of adiabatic shaping of LIPs to achieve population transfer. We have examined the stability of APLIP previously [9], and explained its mechanism in terms of the dynamics of vibrational level crossings. A careful analysis of the wave packet dynamics and the vibrational populations in APLIP allows us to extract the main features necessary to propose new methods for selective population transfer, and to prove that related methods cannot be effective.

We assume that the energetics of the system allow us to consider three separate potential curves coupled by two laser pulses $E_1(t)$ and $E_2(t)$ with center frequencies ω_1 and ω_2. The goal is to selectively invert the electronic population from a single vibrational level on the ground state to a single vibrational level on a final excited state.

The Schrödinger equation for this system, in the Born-Oppenheimer and rotating-wave approximations, is (in atomic units)

$$i\,\frac{\partial}{\partial t}\begin{pmatrix}\psi_1(t)\\ \psi_2(t)\\ \psi_3(t)\end{pmatrix}=\left[\hat{T}+\begin{pmatrix}U_1(x) & -\frac{\Omega_1(x,t)}{2} & 0\\ -\frac{\Omega_1(x,t)}{2} & U_2(x) & -\frac{\Omega_2(x,t)}{2}\\ 0 & -\frac{\Omega_2(x,t)}{2} & U_3(x)\end{pmatrix}\right]\begin{pmatrix}\psi_1(t)\\ \psi_2(t)\\ \psi_3(t)\end{pmatrix}, \tag{1}$$

where $\hat{T}$ is the kinetic energy operator, $U_i(x)$ are the bare electronic potentials, $V_i(x)$, dressed by the photons as $U_1(x) = V_1(x) + \omega_1 + \omega_2$, $U_2(x) = V_2(x) + \omega_2$, and $U_3(x) = V_3(x)$. The Rabi frequencies of the two laser pulses are $\Omega_1(x,t) = E_1(t)\mu_{12}(x)$, $\Omega_2(x,t) = E_2(t)\mu_{23}(x)$.

Let us first examine the properties of the adiabatic potentials dressed by the fields (the LIPs). From a mathematical viewpoint, the LIPs are the potentials derived by diagonalizing the term of the Hamiltonian containing the electronic potentials and the laser couplings. After computing the matrix, $R(x,t)$, such that $R^{-1}\hat{U}R = \hat{U}_{\mathrm{LIP}}$, the Schrödinger equation in the transformed representation reads

$$i\,\frac{\partial}{\partial t}\,\Phi(x,t) = \left(R^{-1}\hat{T}R + \hat{U}_{\mathrm{LIP}} - iR^{-1}\,\frac{\partial R}{\partial t}\right)\Phi(x,t)\,. \tag{2}$$

If the dynamics is both spatially and temporally adiabatic we can assume that $R^{-1}\hat{T}R \approx \hat{T}$, and neglect the last term in Eq. (2). This results in the diagonal equation

$$i\,\frac{\partial}{\partial t}\,\Phi(x,t) = (\hat{T} + \hat{U}_{\mathrm{LIP}})\Phi(x,t)\,. \tag{3}$$

In this representation, the transformed wave packet, $\Phi(x,t) = R^{-1}\psi(x,t)$, evolves adiabatically on the initially populated LIP. As we discuss below, a qualitative understanding of the dynamics can be obtained by a detailed examination of the time-dependent shapes of the LIPs. Note that in the numerical results we make no approximations to the dynamics [that is, we solve Eq. (1) directly].

By using the concept of LIP shaping, we can understand when and why a precise choice of time delay and detuning can control population transfer. As a specific example, we consider a three-state model of the sodium dimer consisting of the $X\,^1\Sigma_g$, $A\,^1\Sigma_u$, and $^1\Pi_g(3p)$ electronic states [10]. We invoke the Condon approximation, and set $\mu_{12} = \mu_{23} = 1$ a.u.

In Fig. 1 we plot the LIPs for the case of three potentials and two pulses. The LIPs are labeled in order of increasing energy as $U_-^{\mathrm{LIP}}(x,t)$, $U_0^{\mathrm{LIP}}(x,t)$, and $U_+^{\mathrm{LIP}}(x,t)$. Depending on the order in which the laser pulses are applied, and the sign of the detuning, the LIPs are composed of different combinations of the field-dressed potentials $U_i(x)$, and evolve asymptotically to different bare states. Four different combinations of time delays (intuitive and counterintuitive) and detunings (red detuning and blue detuning, with respect to the first transition) are illustrated. In this Letter, positive delays imply counterintuitive pulse sequences and positive detunings imply red detunings, in which the energy of $U_2(x)$ lies above the energy of both $U_1(x)$ and $U_3(x)$. To simplify the picture we represent only the initially populated LIP and the LIP that is closest in energy to the initial LIP. The remaining LIP is far enough away in energy that its effect on the dynamics can be neglected. The figure shows four snapshots of the wave packet dynamics at representative times for each case.

Figure 2 presents the population dynamics in the four scenarios in Fig. 1. The results are obtained by integrating the time-dependent Schrödinger equation in Eq. (1) using fields of the form $E_i(t) = \Omega_0 \cosh^{-2}[(t - t_0^{(i)})/\sigma]$, where $\Omega_0 = 0.1$ a.u. and $\sigma = 5.5$ ps. The time at the peak pulse amplitude, $t_0^{(i)}$, is chosen such that the time delay between the pulses is ± 5 ps. The detunings are chosen as

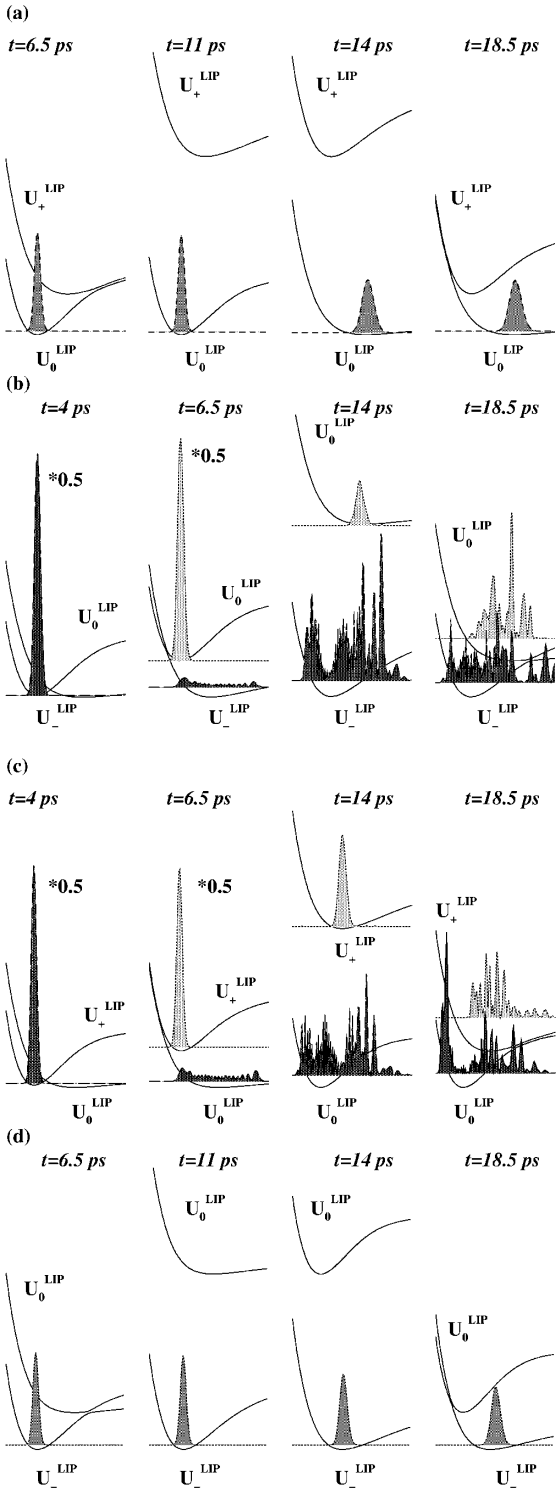

FIG. 1. Four different scenarios for population transfer by shaping of LIPs: Scenario (a) uses a counterintuitive pulse sequence and a blue detuning; scenario (b) uses a counterintuitive pulse sequence and a red detuning; scenario (c) uses an intuitive pulse sequence and a blue detuning; scenario (d) uses an intuitive pulse sequence and a red detuning. Adiabatic wave packets are illustrated schematically for each case. The energy separations between the potentials are drawn to scale.

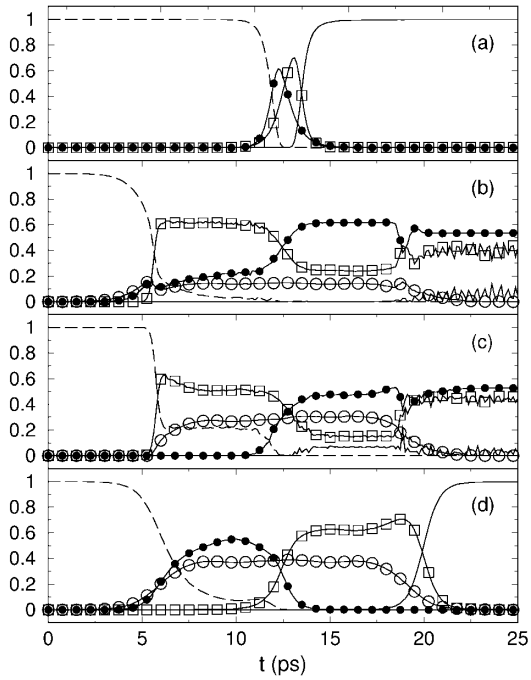

FIG. 2. Population dynamics in the four scenarios depicted in Fig. 1. The solid lines represent the target population ($v'' = 0$ state), the long-dashed lines are the initial population, the solid lines with filled circles are the excited vibrational population on the ground potential (all states with $v \neq 0$), the solid lines with open squares are the excited vibrational population on the final excited electronic state (all states with $v'' \neq 0$), and the solid lines with open circles are the population on the intermediate electronic state.

± 0.025 a.u. To understand the mechanism of population transfer with the various choices of parameters, each panel of Fig. 1 should be considered in parallel with the corresponding panel of Fig. 2.

Figures 1(a) and 2(a) represent the case of blue detuning and counterintuitive pulse sequence. The potential of lowest energy, $U_{-}^{\mathrm{LIP}}(x,t)$, roughly corresponds to $U_2(x)$ and is not shown in the plot. $U_0^{\mathrm{LIP}}(x,t)$ is the initially prepared LIP, and $U_{+}^{\mathrm{LIP}}(x,t)$ is the highest energy LIP. The second pulse, $E_2(t)$, is switched on first, coupling $U_2(x)$ with $U_3(x)$. Because of the dynamic Stark shift the coupling affects the right well of $U_0^{\mathrm{LIP}}(x,t)$, increasing its energy and separating it from $U_{-}^{\mathrm{LIP}}(x,t)$. This process raises the energy barrier to wave packet motion, and as a result, the wave packet does not move. After some time, $E_2(t)$ decreases in intensity while $E_1(t)$ increases, so the first well rises and the second well falls. Eventually, the inner barrier is suppressed to the point that the wave packet moves from the left well [corresponding to displacement of the wave packet from the equilibrium to the repulsive barrier in $U_1(x)$] to the right well [corresponding to displacement of the wave packet from the repulsive barrier in $U_3(x)$ to the new equilibrium position]. This is shown in the second snapshot in Fig. 1(a). In an eigenstate representation of the bare Hamiltonian, the wave packet movement in this case would be described as a sequence of Raman Stokes, two-photon absorption, and Raman anti-Stokes processes. At final times both pulses are switched off and the energy barrier is restored, thus preventing the recrossing of the wave packet to the ground state. If the dynamics is fully adiabatic, the number of nodes in the wave function does not change. Therefore, if, for example, the initial vibronic state is $v = 0$, the final state is $v'' = 0$.

Scenario 1(b) also uses a counterintuitive pulse sequence but now the first pulse is detuned to the red of the resonance. Thus $U_2(x) \approx U_{+}^{\mathrm{LIP}}(x,t)$ and the wave function is initially in $U_{-}^{\mathrm{LIP}}(x,t)$, and not in $U_0^{\mathrm{LIP}}(x,t)$, as in scenario 1(a). Once again, the Stark shift induced by $E_2(t)$ separates $U_3(x)$ from $U_2(x)$, but in this case the energy of the right well in $U_{-}^{\mathrm{LIP}}(x,t)$ is lowered and therefore the barrier to the left well is lowered. This causes the wave packet to move from one well to the other. Since this movement occurs at an early stage in the process, when the pulses are not intense enough for the process to be fully adiabatic, the avoided crossing is small and substantial nonadiabatic crossing occurs between $U_{-}^{\mathrm{LIP}}(x,t)$ and $U_0^{\mathrm{LIP}}(x,t)$. This results in transfer of part of the wave packet from $U_{-}^{\mathrm{LIP}}(x,t)$ to $U_0^{\mathrm{LIP}}(x,t)$ [see the snapshots at 4 ps and at 6.5 ps in Fig. 1(b)]. This "horizontal" displacement of the wave packet does not preserve the shape of the initial wave function. At intermediate times, the barrier rises again, and at final times the Stark shift induced by $E_1(t)$ lowers the energy of the barrier, thus allowing the re-crossing of the wave packet to the original potential. The overall result, as seen in Fig. 2(b), is inefficient population transfer, with no selectivity on the final state.

Using similar arguments we can see that scenario 1(c), with blue detuning and an intuitive pulse sequence, leads to inefficient, nonselective population transfer. In this case the initial wave function is prepared in $U_0^{\mathrm{LIP}}(x,t)$, and the sequence of Stark shifts enables two crossings of the wave packet, thus partially returning it to its initial position. The lack of adiabaticity once again leads to considerable delocalization of the final wave packet. In contrast, scenario 1(d), which uses an intuitive sequence and red detuning, is perfectly suited for selective population transfer. The wave function is originally excited to $U_{-}^{\mathrm{LIP}}(x,t)$. The Stark shift induced by $E_1(t)$ causes the energy of the internal barrier of $U_{-}^{\mathrm{LIP}}(x,t)$ to rise, because the repulsion between the surfaces increases the depth of the first well. At intermediate times, the barrier is suppressed and the wave packet is transferred to the right well, which correlates to $V_3(x)$ at asymptotic times. Just as in scenario 1(a), the process is fully adiabatic, and the population transfer is selective.

Figures 1 and 2 show that selective population transfer can be attained by two quite different scenarios. One of these schemes, [scenario 1(a)], is equivalent to the APLIP method described previously [8]. The second [scenario 1(d)] is a variant of APLIP that has not been demonstrated previously. The numerical results indicate that both scenarios result in selective population transfer to the ground vibrational level of the second excited electronic state. Of course, since the process is performed on different LIPs

$[U_0^{\mathrm{LIP}}(x,t)$ or $U_-^{\mathrm{LIP}}(x,t)]$ there are differences in the dynamics. With the counterintuitive sequence in scenario 1(a), the effect of the pulses is to act indirectly on the wave packet during a very short time, while in the intuitive sequence in scenario 1(d), the first pulse shapes the LIP in the region directly in which the wave packet is located. Therefore, both Raman processes operate for longer times in scenario 1(d), and a larger amount of population is temporarily transferred to the first excited state [nearly 35% compared to less than 1% in scenario 1(a)]. The other two scenarios, in contrast, result in recrossing of the wave packet to the ground state. During this recrossing the system loses selectivity, and several vibrational levels on both the ground state and the excited state are populated. Once again, the vibrational dynamics are quite different in scenarios 1(b) and 1(c).

The examples presented above indicate that selective population transfer can be achieved with a pair of properly timed, properly detuned ultrafast laser pulses. An alternative method to achieve selective population transfer is via the use of stimulated Raman adiabatic passage (STIRAP) [11]. We mention briefly some of the similarities and differences between STIRAP and the present method. STIRAP employs a counterintuitive sequence of pulses as in scenario 1(a) discussed above. However, STIRAP depends on the ability to identify a single vibrational level on the first excited state, $V_2(x)$, that couples efficiently to the chosen vibrational levels on the ground and final states. A potential difficulty with such a scheme arises when the equilibrium geometries of the potentials have large displacements. In this case, the Franck-Condon factors for the transition may be negligible, which makes the process inefficient.

At first glance STIRAP can overcome the absence of strong coupling between the initial and final states by using intense laser pulses. However, increasing the intensity activates Raman processes that compete with two-photon absorption if the corresponding Rabi frequencies exceed the vibrational quanta. This causes the route to the target state to branch into several competing processes, and results in a final yield to the desired state that may be quite small. We have checked that this is, indeed, the case for population transfer in the picosecond regime between the ground and the $C\,^1\Sigma_u(v'' = 0)$ state in the sodium dimer. A numerical simulation indicates a yield of less than 1% in a STIRAP-type method for 20 ps pulses with an amplitude of 5×10^{-4} a.u. (adiabaticity parameter [11] of about 60). The results cannot be improved by using stronger fields, unless the temporal width of the pulses is increased considerably (to the nanosecond regime). In contrast, the APLIP methods discussed here utilize the Franck-Condon factors of *all* of the vibrational levels of the intermediate electronic state and are therefore not as sensitive to the magnitude of any particular Franck-Condon factor.

In conclusion, we have shown that LIP shaping is a powerful and robust method for selective population transfer. Its only limitations arise from the requirement of strong pulses in the picosecond regime. There is always a risk, with such pulses, that additional, competing pathways such as ionization and multiphoton processes can diminish the selectivity and efficiency of the population transfer. The duration of the pulses cannot be decreased to the femtosecond regime, because such pulses would cause the rapid excitation of a superposition of many energy levels, which would spoil the selectivity. A potential limitation results from the symmetry requirement implicit in the conservation of the vibrational quantum number. That is, the final vibrational state must have the same number of nodes as the initial vibrational state. In practice this may, in fact, be an advantage, since the selectivity of the system does not depend on the energetics and is given *a priori* by the shape of the initial wave function. Population transfer to a different final state requires an initial population of the appropriate vibrational level on the ground state, perhaps via nanosecond STIRAP. Although the numerical results presented here employ simple models, preliminary, more realistic, calculations make us confident that the method is worthy of experimental verification. In a following paper [12] we present more complete results of the LIP dynamics and test the numerical approximations made in this work.

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