Tailoring of vibrational state populations with light-induced potentials in molecules

M. Rodriguez

Helsinki Institute of Physics, PL 9, FIN-00014 Helsingin yliopisto, Finland
and Department of Electrical Engineering, Helsinki University of Technology, PL 9400, FIN-02015 TKK, Finland

K.-A. Suominen

Helsinki Institute of Physics, PL 9, FIN-00014 Helsingin yliopisto, Finland
and Department of Applied Physics, University of Turku, FIN-20014 Turun yliopisto, Finland

B. M. Garraway

SCOAP and Centre for Theoretical Physics, CPES, University of Sussex, Falmer, Brighton, BN1 9QJ, United Kingdom

We propose a method for achieving highly efficient transfer between the vibrational states in a diatomic molecule. The process is mediated by *strong* laser pulses and can be understood in terms of light-induced potentials and their vibrational eigenstates. In addition to describing a specific molecular system, our results show how, in general, one can manipulate the populations of the different quantum states in double-well systems.

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I. INTRODUCTION

Quantum control of molecular processes has recently opened new possibilities for controlling chemical processes, and also for understanding the multistate quantum dynamics of molecular systems. With strong and short laser pulses one can create quantum superpositions of vibrational and continuum states, i.e., wave packets, which often propagate like classical objects under the influence of molecular electronic potentials [1]. Typically in spectroscopy one induces with laser light population transfer between individual vibrational states, and describes the process using Franck-Condon factors, perturbation theory, and a very truncated Hilbert space for the molecular wave functions. If the laser light comes in as a very short pulse we expect to couple many vibrational states because of the broad spectrum. However, we show that in theory it is possible to start from a single vibrational state, and end up selectively on another single vibrational state, with very high efficiency, even when one uses strong and fast laser pulses. The standard theoretical approach to such systems is wave-packet dynamics, and we have used it in the following study.

We have previously discussed how one can transfer the vibrational ground-state population of one electronic state to the vibrational ground state of another electronic state [2]. This process was called adiabatic passage in light-induced potentials (APLIP). The light-induced potentials, which depend on time because of the time dependence of the laser-pulse envelopes, provide a useful description of the process (see e.g., Ref. [3] and references therein). Here we use the same kind of light-induced potentials to describe and understand transfer processes between excited vibrational states. However, we shall see that the process is more complicated than the simple adiabatic following assumed in APLIP. The complete understanding requires one to study the instantaneous vibrational eigenstates of the time-dependent light-induced potentials. It turns out that the simple-looking time

evolution of the molecular system consists of a nontrivial interplay between diabatic and adiabatic behavior.

Our presentation takes place as follows. In Sec. II we describe the electronic states of the sodium dimer, which we use to demonstrate the vibrational state tailoring process. It should be emphasised that the process is very general and we use the sodium dimer merely as a convenient example. In Sec. III we show how the dynamics of a system of three electronic molecular states interacting with two laser pulses can be described with the light-induced potentials. We also review the previous APLIP work [2]. Then in Sec. IV we present the numerical results showing the tailoring of vibrational state populations of the electronic states, and show how it can be understood in terms of the instantaneous vibrational eigenstates. Finally, Sec. V concludes the paper with some discussion on the general aspects of our results.

II. SODIUM DIMER MODEL

To demonstrate the tailoring of the vibrational state populations we have chosen a set of Na dimer potentials, shown in Fig. 1(a) [2]. The three electronic states are coupled in a ladder formation by two laser pulses. Instead of describing the system in terms of the vibrational states and Franck-Condon factors, we consider only the electronic state wave functions, $\Psi_i(R,t)$, $i=X,A,\Pi$. If we apply the rotating wave approximation, we can ''shift'' the $X^1\Sigma_g^+$ and $2^1\Pi_g$ state potentials by the corresponding laser photon energies. Then we obtain the situation shown in Fig. 1(b), after a suitable redefinition of the energy zero point. The resonances between the electronic state potentials now become curve crossings. The evolution of the three wave functions $\Psi_i(R,t)$ is given by the time-dependent Schrödinger equation with the Hamiltonian

$$H=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}\mathcal{I}+\mathcal{U}(R,t),\tag{1}$$

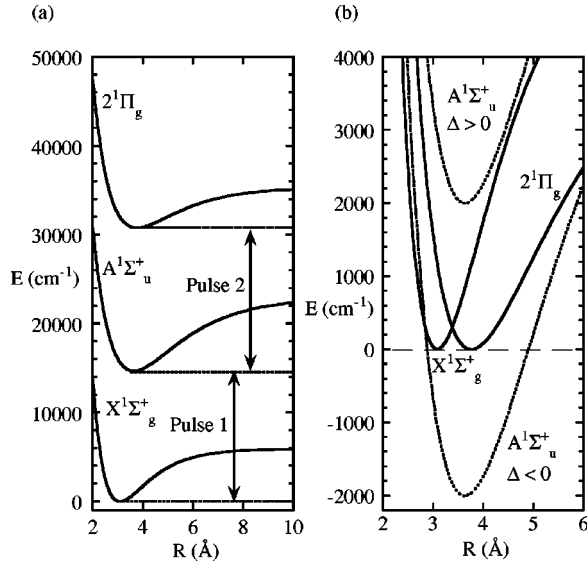FIG. 1. (a) The three Na$_2$ potential energy surfaces used in our calculations: $X^1\Sigma_g^+$, $A^1\Sigma_u^+$, and $2^1\Pi_g$. (b) The shifted potentials. Here we have set $\Delta = \Delta_1 = -\Delta_2$, [see Eq. (2)] and show the position of the intermediate $A^1\Sigma_u^+$ state (dotted line) with respect to the other two electronic states (solid lines) for $\hbar\Delta = \pm 2000$ cm^{-1}.

where R is the internuclear separation, m is the reduced mass of the molecule, and the electronic potentials and couplings are given by

$$\mathcal{U}(R,t) = \begin{bmatrix} U_X(R) & \hbar\Omega_1(t) & 0 \\ \hbar\Omega_1(t) & U_A(R) + \hbar\Delta_1 & \hbar\Omega_2(t) \\ 0 & \hbar\Omega_2(t) & U_\Pi(R) + \hbar(\Delta_1 + \Delta_2) \end{bmatrix}.$$

(2)

Here $U_X(R)$, $U_A(R)$, and $U_\Pi(R)$ are the three potentials, Δ_1 and Δ_2 are the detunings of the two pulses from the lowest points of the potentials [dashed lines in Fig. 1(a)], and $\Omega_1(t) = \mu_{XA}E_1(t)/\hbar$, $\Omega_2(t) = \mu_{A\Pi}E_2(t)/\hbar$ are the two Rabi frequencies. We have assumed for simplicity that the two dipole moments are independent of R and we have used Gaussian pulse shapes, $\Omega_i(t) = \Omega \exp\{-[(t-t_i)/T]^2\}$, $i = 1,2$. Our wave-packet dynamics approach consists of solving Eq. (1) numerically using the split-operator method and Crank-Nicholson evaluation of the kinetic-energy term [1].

III. MODELLING WITH LIGHT-INDUCED POTENTIALS

The light-induced potentials are obtained by diagonalizing the potential term (2). For these potentials the curve crossings become avoided crossings. It is easy to see from Fig. 1(b) that in the absence of the pulses (or when they both are weak) one of the light-induced states corresponds, at low energies, to a double-well structure formed by the $X^1\Sigma_g^+$ and $2^1\Pi_g$ electronic state potentials. In Fig. 1(b) this corresponds to the lower part of the two solid curves and we shall call this the active eigenstate. If we choose $\Delta_1 = -\Delta_2 \equiv \Delta$, the bottoms of the two wells are on the same level initially and finally [as in Fig. 1(b)].

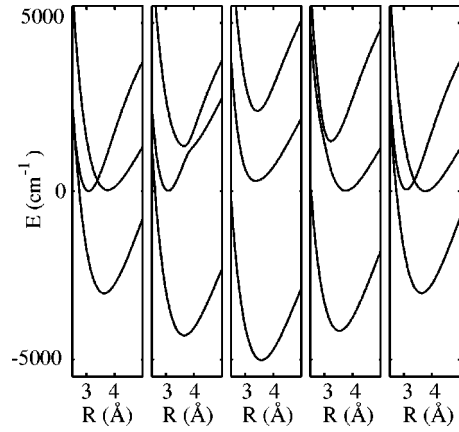In Ref. [2] we showed that, if the pulses are applied in a

FIG. 2. The form of the three light-induced potentials at selected times during the interaction with the two pulses, for $\hbar\Delta = -3000$ cm^{-1} and $\hbar\Omega = 3000$ cm^{-1}. The active eigenstate is the one with its minima always closest to the energy zero point. Note that in the first and last frame both pulses are weak (the asymptotic case); although the potentials seem to cross around 3.3 Å, there is, in fact, an avoided crossing.

counterintuitive order ($t_1 > t_2$), the double-well structure will disappear as the bottom of the (initially empty) well on the right moves up and vanishes, when $\Delta < 0$. [In Fig. 1(b) this is seen to be because of a repulsion between the $2^1\Pi_g$ and $A^1\Sigma_u^+$ ($\Delta < 0$) state]. After this the left well broadens and moves to the right. Finally the double-well structure is re-established as the pulses reduce in intensity. This behavior is demonstrated in Fig. 2. If we now consider that the ground vibrational state of the left well is initially populated, that population would follow the light-induced potential and be transformed smoothly into the ground-state wave function of the right well. This is APLIP, and the smooth change in the total wave function is demonstrated in the contour plot in Fig. 3(a).

The sign of Δ determines the evolution of the light-induced potential. For negative Δ we obtain the APLIP situation, but for positive Δ the right well drops down at first, instead of disappearing. In this case the APLIP situation is not obtained. Instead, the wave packet spreads violently to cover a wide spatial region.

One is tempted to associate the APLIP process with stimulated Raman adiabatic passage (STIRAP) [4], and consider the active light-induced potential as a dark state [5], which, because of the counterintuitive pulse order, remains uncoupled from the other states. It is true that during the APLIP process the intermediate state ($A^1\Sigma_u^+$) population remains very small as expected for STIRAP. However, the process is not the same as STIRAP, because the strength of the atom-light coupling, i.e., Rabi frequency, becomes much larger than the vibrational spacing; it is not possible to isolate only a few energy levels. Furthermore, in a STIRAP process there would not be a smooth transport of the wave packet in Fig. 3(a) because only two simple vibrational eigenfunctions should be involved (further discussion can be found in Ref. [6]).

STIRAP is also considered to be an adiabatic process, which is not strictly the case for Fig. 3. We can see this by considering the asymptotic (initial and final) vibrational
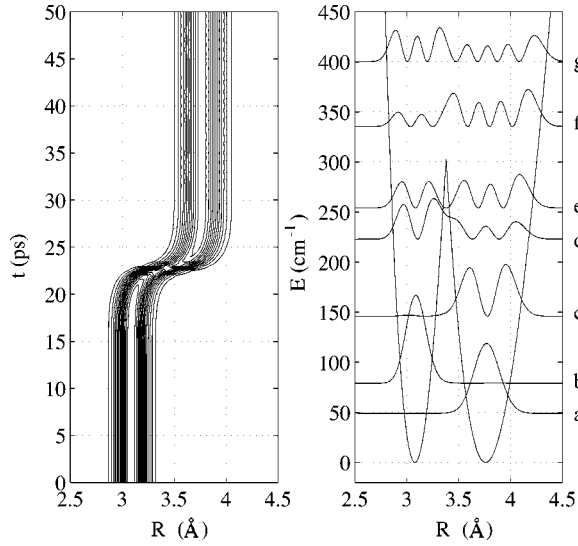
FIG. 3. (a) The APLIP process for $\hbar\Delta = -3000$ cm^{-1}, $\hbar\Omega = 2000$ cm^{-1}, $t_1 = 25.5$ ps, $t_2 = 20.5$ ps, and $T = 5.5$ ps. The contour plot shows the time evolution of the total probability distribution $|\Psi(R,t)|^2 = \Sigma_i|\Psi_i(R,t)|^2$ (wave packet). (b) The active light-induced state (independent of Δ at low energies) when the pulses are absent ($\Omega = 0$). We also show the seven lowest vibrational eigenstates $|\phi_i(R)|^2$ of the potential (labeled with a, b etc.). The left well corresponds to the $X^1\Sigma_g^+$ electronic state, and the right one to the $2^1\Pi_g$ electronic state.

FIG. 4. (a) The vibrational state tailoring with $\hbar\Delta = 2010$ cm^{-1}, $\hbar\Omega = 733$ cm^{-1}, $t_1 = 25.5$ ps, $t_2 = 20.5$ ps, and $T = 5.5$ ps. (b) The time-dependent eigenenergies of the five lowest vibrational states of the active light-induced potential for the situation shown in (a). [Note that for $t \lesssim 15$ ps and $t \gtrsim 35$ ps the eigenstates match those seen in Fig. 3(b).] Diabatic transitions between the eigenstates are marked with circles.

eigenstates of the active light-induced potential, shown in Fig. 3(b). The lowest eigenstates (a,b,c) clearly correspond to the individual vibrational states of the electronic potentials. In STIRAP we should start with the lowest state on the left, b, and we would expect it to evolve adiabatically into the lowest state on the right, a, though not in the smooth way seen for the APLIP process in Fig. 3(a). However, if the evolution were *truly* adiabatic the population would remain in the left well; by the definition of adiabatic following, the system cannot move from one eigenstate to another.

In fact, APLIP is possible because, as the right well rises up, and the right well wave function with it, the system jumps diabatically from eigenstate b to the eigenstate a. The pulses are too weak to force the system to jump from the left well to the right well at this point, which would be the case for adiabatic following. In other words, the system moves through the avoided crossing of the eigenstates a and b diabatically. Thus the population remains in the left well as the right well vanishes (see the second frame of Fig. 2). As long as the energy barrier between the two wells is thick and tall enough, the crossing of vibrational eigenenergies remains diabatic and the wave packet (left well vibrational ground state) can be channeled from left to right smoothly (APLIP). We shall encounter this phenomenon again later in Sec. IV.

There always has to be at least one such diabatic crossing, but if there is only one, it could come at the start, or the end, of the time evolution depending on whether the initial or final vibrational state is lower in energy. Thus the interesting processes mediated by the light-induced potentials are different from STIRAP, and they are not obtained by perfect adiabatic following.
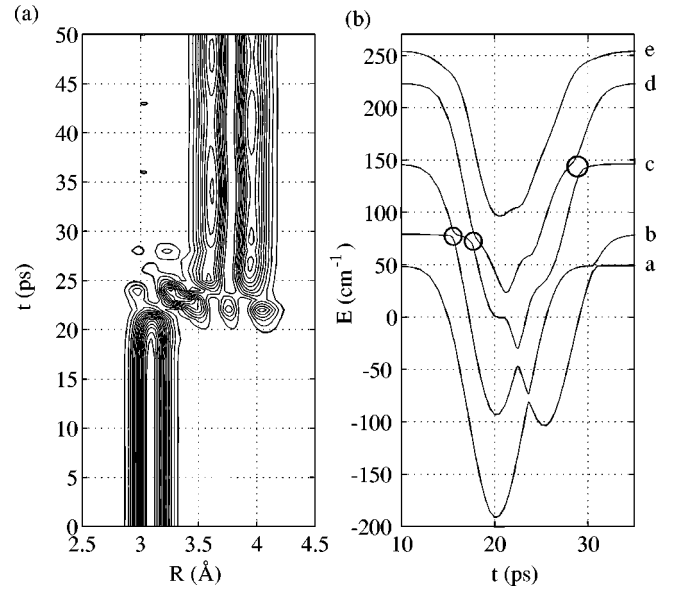
IV. PROCESSES INVOLVING EXCITED VIBRATIONAL STATES

We will now turn to new situations where excited vibrational states become involved. We will see that a positive detuning Δ is crucial for this case. Because there is no coupling between the states at the initial and final times, Fig. 3(b) displays the vibrational eigenstates, at the initial and final times, for positive detuning as well as negative detuning. We choose the positive detuning $\hbar\Delta = 2010$ cm^{-1} for the time evolution shown in Fig. 4(a), where $\hbar\Omega = 733$ cm^{-1} and $t_1 - t_2 = T = 5.5$ ps. We denote the vibrational quantum number of the states in the electronic potential with ν, and indicate with the terms ''left well'' and ''right well,'' whether these states correspond to the initial state ($X^1\Sigma_u^+$), or the final state ($2^1\Pi_g$), respectively. We transfer the $\nu = 0$ state on the left well into the $\nu = 1$ state on the right well. The process is very efficient: the occupation probability of the right well ($2^1\Pi_g$ state) in the end is 94%. Clearly the crucial moment is around $t = 20$ ps, where the original single-peak distribution extends to the right and forms temporarily a four-peaked distribution over the combined well system. Also, around $t = 25$ ps, the four-peak structure compresses into the two-peak structure located on the right well.

In order to understand the process we have now calculated the time dependence of the eigenenergies of the active light-induced potential [seen for initial and final time in Fig. 3(b)]. The figure shows clearly that if the evolution is fully adiabatic, no change of ν can occur during the time evolution because there are no crossings of eigenenergies. This also means that no change of well is possible either. However, we
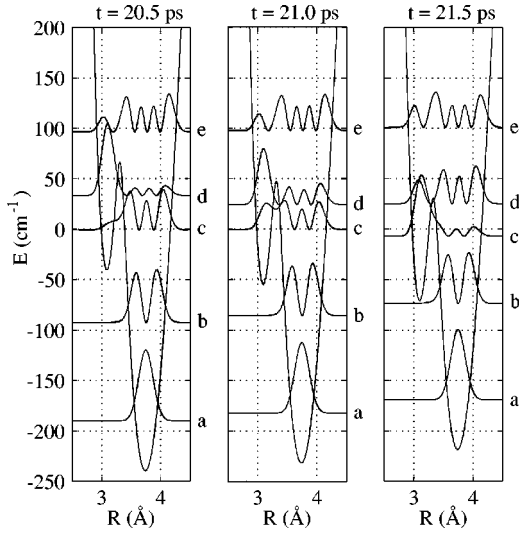
FIG. 5. The behavior of the eigenstates of the active light-induced potential in the situation of Fig. 4 around $t=21$ ps. The eigenstate d deforms within 1 ps from the initial single-peak structure into a four-peak one. An inverse process happens to the eigenstate c. In the diabatic situation the system would follow the single-well eigenstates, thus jumping from d to c. However, here the system follows d adiabatically instead.

FIG. 6. The behavior of the eigenstates of the active light-induced potential during the diabatic transfer between the eigenstates b and c around $t=15$ ps. The eigenstate b deforms very quickly, within 1 ps, from the single-peak on the left well to the two-peak state on the right well. The eigenstate c experiences the inverse process. But in reality the system remains in the first well, jumping diabatically from state b to c.

do see several avoided crossings between the eigenenergies and the point is that when the pulses are weak, these crossings are passed diabatically, and when the pulses are strong they are passed adiabatically.

In our example, Fig. 4(b), the eigenstate b corresponds initially, and finally, to the lowest vibrational state of the left well (i.e., the state populated initially in our calculation) as may be confirmed by inspecting Fig. 3(b). During the time evolution the system passes the two first avoided crossings diabatically, but for $t>20$ ps it follows nearly adiabatically the eigenstate d. We mark the diabatic crossings with rings in the figure. Just before $t=30$ ps the system moves diabatically onto the eigenstate c, which asymptotically corresponds with the $\nu=1$ state on the right well [see again Fig. 3(b)]. In Fig. 5 we show the change at the crucial moment around $t=21$ ps. The transition from a narrow single-well wave function into a wide combined two-well wave function takes place very quickly. A fascinating aspect is that the evolution of the total wave function still follows the eigenstate d of the active light-induced potential. A similar adiabatic following happens also near $t=25$ ps when the eigenstates c and d again approach each other.

For contrast, Fig. 6 shows what happens at the first diabatic crossing, around $t=15$ ps. The change in the eigenstates from one well to the other takes place within 1 ps. Since both wells are strongly separated, such a transfer is unlikely to happen and the system evolves diabatically. This is the same situation as discussed in Sec. III for the beginning of the APLIP process. Here the system jumps from the eigenstate b to the eigenstate c, i.e., the actual state is a single peak on the left well during the process even though the eigenstates change dramatically.
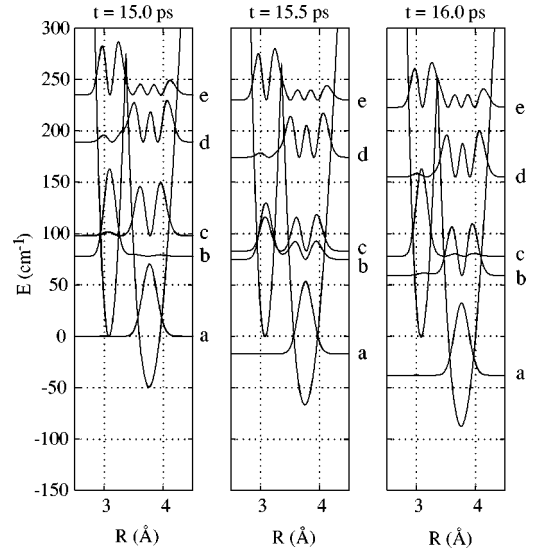
The example given here is not unique. By allowing Δ_1

$\neq -\Delta_2$ we have a very good handle in choosing which single-well states are paired into a combined well state. In Fig. 7 we show two other examples. They demonstrate that the process does not require the initial state on the left to be $\nu=0$, and the process can be used also to change ν but keep the initial and final well the same [7].

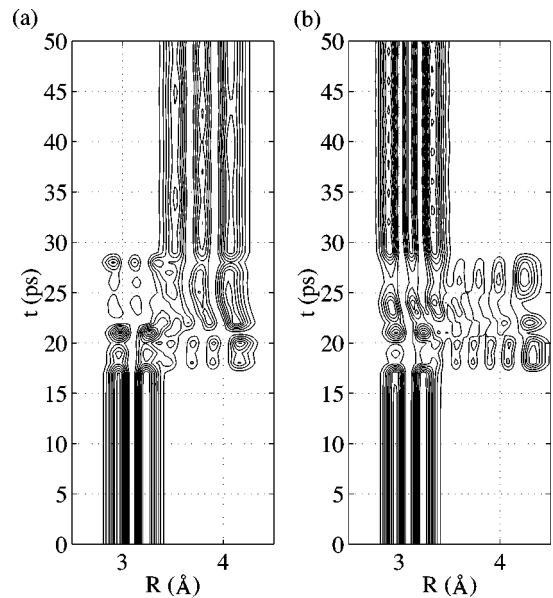In the region where both pulses are strong the adiabatic

FIG. 7. The state tailoring process with $\nu=1$ in the left well as the initial state. (a) $\nu=2$ in the right well as the final state. Here $\hbar\Delta_1=2010$ cm^{-1} and $\hbar\Delta_2=-1960$ cm^{-1}. (b) $\nu=2$ in the left well as the final state. Here $\hbar\Delta_1=2010$ cm^{-1} and $\hbar\Delta_2=-2160$ cm^{-1}.

following of a single vibrational eigenstate is not complete. Small oscillating contributions appear in the final state. The contour plots tend to emphasise these oscillations. For example, in the particular case of Fig. 4(a), only about 2% probability of diabatic transfer creates these oscillations.

V. CONCLUSIONS

We have shown how, even with strong and short laser pulses one could perform very selective and yet efficient tailoring of vibrational state populations in molecules. We have used Gaussian pulse shapes, but with other pulse shapes it might be possible to achieve even better control of the adiabaticity at different avoided crossings between the eigenstates. The examples we have given show two advantages over the previously described APLIP process. Firstly, having $\Delta > 0$ (a region in which APLIP does not work) moves the central frequencies of the two laser pulses away from each other. Secondly, the required intensities are clearly smaller as we mainly need to shift the potentials, rather than deforming them strongly. Thus the transfer processes may be achievable with peak powers of less than 1 TW/cm^2. This is quite accessible experimentally, although, as discussed in Ref. [2], we have treated only a three-level system here. We expect this to be a fair approximation, given that the pulses must be a least a little longer than typical vibrational time scales (reducing bandwidth). Level repulsion can then be expected to help the three-level approximation provided there are no adiabatic crossings with unwanted levels.

If we were to describe the process of tailoring vibrational state populations using the *vibrational* state basis of the three electronic potentials, the treatment would involve complicated transfer processes between a large number of states. Our presentation shows that the process can be understood very well in terms of the light-induced potentials, and their time-dependent vibrational eigenstates. Furthermore, this description also allows one to identify how the system parameters should be set in order to achieve specific outcomes.

The main ingredient is establishing the right balance between the adiabatic following of the time-dependent vibrational eigenstates, and nonadiabatic transfer between them at avoided crossings. We have discussed the situation in a molecular multistate framework, but in the light-induced potential description the relevant process really takes place within a general two-well potential structure. Thus our observations hold also for any two-well structure, where the barrier height and the well depths can be controlled time dependently in similar manner.

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[7] A rather obvious extension of APLIP is to start with a $\nu > 0$ state, and move from the left well to the right one while preserving ν.