Adiabatic Passage by Light-Induced Potentials in Molecules

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(Received 3 September 1997)

We present the process of adiabatic passage by light-induced potentials for transferring a wave packet from one molecular potential to the displaced ground vibrational state of another. The process uses a counterintuitive sequence of light pulses to couple three molecular states. It shares many features with the process of stimulated Raman adiabatic passage, such as high efficiency and insensitivity to pulse parameters. However, in the former there is no two-photon resonance, and the main mechanism for the transport of the wave packet is a light-induced potential.   [S0031-9007(97)05254-X]

Femtosecond pulses have recently opened the possibility to create, observe, and control the internal dynamics of molecules [1,2]. Typically, one has studied the pump-probe situation, where a molecular wave packet, i.e., a coherent superposition of vibrational states, has been created by the first pulse, and a second pulse probes the subsequent evolution of the wave packet. Alternatively, one can observe the dissociation process directly. In more subtle cases, such as the pump and dump schemes, the final result can be some special molecular bound state instead of dissociation. Such manipulations provide new understanding of molecular dynamics and chemical reactions. Also, they present intriguing demonstrations of wave packet dynamics and time-dependent quantum mechanics in general.

The purpose of this Letter is to demonstrate (theoretically) a mechanism for the transfer of a stationary ground state vibrational wave packet to a *stationary and displaced* excited state wave packet through an intermediate state which is not significantly populated during the process. The overall effect is symbolically represented by the diagonal arrow in Fig. 1. Of course, we can change from a wave packet picture of the process to a picture in terms of the vibrational levels, in which case Fig. 1 illustrates a process where the population of the $\nu = 0$ vibrational level of the ground state is directly transferred to the $\nu'' = 0$ vibrational level of the second excited state. The overall effect appears as a violation of the Franck-Condon principle, which can be simply stated as saying that there should only be vertical transitions between vibrational states in a molecule, at least over short times. Thus the diagonal transition seen in Fig. 1 should not be allowed. It is further inhibited by the fact that the overlap between the initial and final wave functions is very small (the Franck-Condon overlap). This is because the initial wave packet is displaced over a distance of about seven times its width for the example of Fig. 1. Of course, there

is no real violation of the Franck-Condon principle; we manipulate the molecular states on time scales close to, but longer than the vibrational time scales.

To illustrate the process we have chosen the sodium dimer, a molecule which has already been subjected to much study in the field of wave packet dynamics, and which opens the prospect of an experiment to test the ideas in this Letter. Following Refs. [3] we have chosen our three states so that the ground state is the $X^1\Sigma_g^+$ of Na_2, the first excited state is the $A^1\Sigma_u^+$ state, and the second excited state is the $2^1\Pi_g$ state. Data for the molecular potentials have been gathered from Refs. [3,4] and these data are used in a numerical calculation of the dynamics of the wave packet during the interaction of the system with two laser pulses.
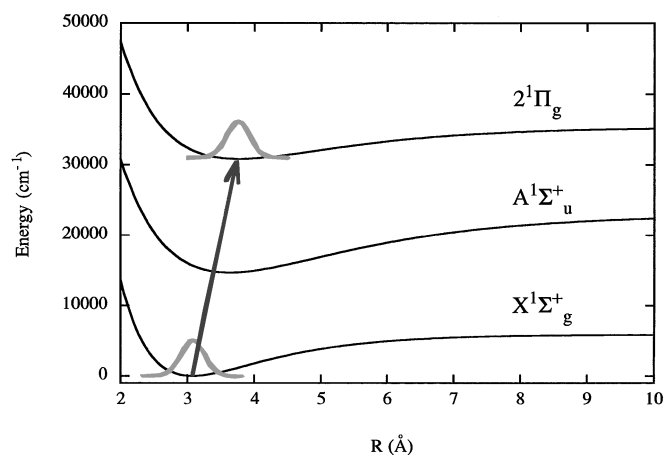

FIG. 1. The three Na_2 potential energy surfaces used in our calculations: the $X^1\Sigma_g^+$ ground state, the $A^1\Sigma_u^+$ state as the first excited state, and the $2^1\Pi_g$ as the third state. The diagonal sloping arrow indicates the overall effect of the two laser pulses used.

In terms of the electronic potentials the Hamiltonian for the vibrational motion of the molecule is

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

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

$$\mathcal{U}(R,t)$$
$$= \begin{bmatrix} U_X(R) + \hbar\delta_1 & \hbar\Omega_1(t) & 0 \\ \hbar\Omega_1(t) & U_A(R) & \hbar\Omega_2(t) \\ 0 & \hbar\Omega_2(t) & U_\Pi(R) + \hbar\delta_2 \end{bmatrix}. \quad (2)$$

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, 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 solve the time-dependent Schrödinger equation with Hamiltonian (1) by a numerical method (see, e.g., Ref. [2]).

Figure 2 shows an example of the wave packet dynamics following the coupling of two pulses between each
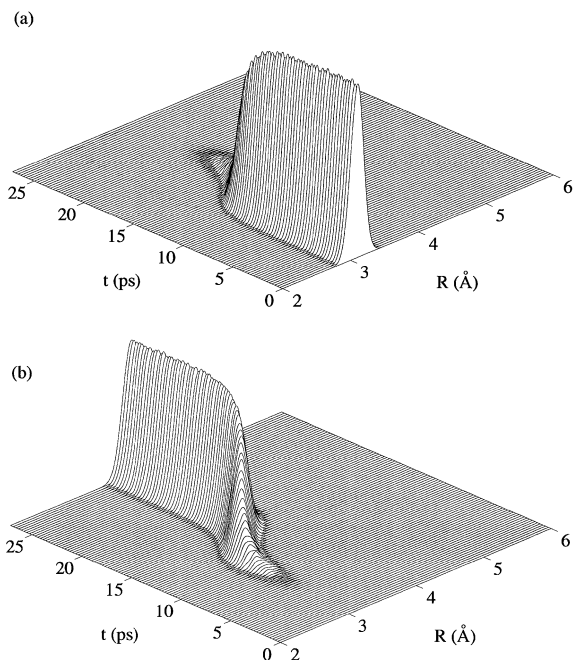

(a)

(b)

FIG. 2. The wave packet dynamics on (a) the $X^1\Sigma_g^+$ ground state and (b) the target state $2^1\Pi_g$. The wave packet motion has been determined from a fully quantum mechanical calculation. In (a) the ground state wave packet disappears when the two pulses arrive at $t = 10.8$ ps and 16.3 ps. In (b) we see the slow and steady appearance of the wave packet in the $2^1\Pi_g$ state. Note the steady displacement of the wave packet as it arrives adiabatically to the bottom of the lowest vibrational state of the $2^1\Pi_g$ state. Both pulses are red detuned from the bottom of the potential energy surface by 2200 cm^{-1} and have a width of 5.42 ps.

pair of molecular states. In Fig. 2(a) we see at $t = 0$ the initial ground state wave packet, located at the equilibrium position of 3.08 Å, in the $X^1\Sigma_g^+$ potential. When the two Gaussian laser pulses (with peak intensities of 3 and 6 TW/cm^2) act on the molecule we see the disappearance of the wave packet from the $X^1\Sigma_g^+$ state, while it is also displaced to the right (to larger distances). As the wave packet disappears from the $X^1\Sigma_g^+$ state it appears on the excited $2^1\Pi_g$ state [see Fig. 2(b)], still being displaced to longer bond lengths as it appears. When the laser pulses have been completed, the wave packet is left in the $2^1\Pi_g$ state without any vibrational excitation (there is no motion of the wave packet).

During the process seen in Fig. 2 the $X^1\Sigma_g^+$ and $2^1\Pi_g$ states exchange their population while the population of the $A^1\Sigma_u^+$ state remains very low at all times. The process is nearly 100% efficient in transferring population from the $X^1\Sigma_g^+$ state to the $2^1\Pi_g$ state. This efficiency remains high over a wide range of pulse parameters.

The process we have described uses a counterintuitive pulse sequence: the pulse nearly resonant with the $X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ transition is applied *after* the pulse nearly resonant with the $A^1\Sigma_u^+ \rightarrow 2^1\Pi_g$ transition. However, the process is not the same as the conventional STIRAP [5–7] (stimulated Raman adiabatic passage) process, already seen in molecular systems [6], for both trivial and fundamental reasons. The most trivial difference with the existing experiments is the linkage pattern; the ladder system we consider (Fig. 1) has a different linkage pattern from the Raman type Λ system after which STIRAP is named. In the absence of spontaneous emission [8], these different linkage patterns do not affect the dynamics in the case of atomic systems [7].

Because we utilize a ladder system it makes sense to consider a transition from $X^1\Sigma_g^+$ ($\nu = 0$) to $2^1\Pi_g$ ($\nu'' = 0$), i.e., from the ground vibrational state of the lowest electronic state to the ground vibrational state of the highest electronic state in our three-level system. In a Λ-type Raman scheme this would not make sense as STIRAP is then used to create an excited vibrational state ($\nu \neq 0$) from the ground state ($\nu = 0$) within the same electronic state of the molecule.

Conventional STIRAP utilizes a two-photon resonance condition. For example, a suitable Hamiltonian for STIRAP in an atomic ladder system is

$$H_a = \begin{bmatrix} 0 & \hbar\Omega_1(t) & 0 \\ \hbar\Omega_1(t) & \hbar\Delta & \hbar\Omega_2(t) \\ 0 & \hbar\Omega_2(t) & 0 \end{bmatrix}, \qquad (3)$$

where Δ is the two-photon resonant laser-atom detuning, and Ω_1 and Ω_2 are the Rabi frequencies of the pump pulse and Stokes pulse. If the pump and Stokes pulses change sufficiently slowly, we can consider the process to be adiabatic. Then we can utilize the instantaneous

eigenstate

$$\psi_z(t) = \frac{1}{\sqrt{\Omega_1^2(t) + \Omega_2^2(t)}} \begin{pmatrix} \Omega_2(t) \\ 0 \\ -\Omega_1(t) \end{pmatrix} \qquad (4)$$

to achieve the transfer directly from state 1 to state 3. We note that the state ψ_z is for all t an exact eigenstate of H_a, Eq. (3), with eigenvalue zero (sometimes called a "dark state" [9]). If the pulses are in the counterintuitive order, i.e., $\Omega_2(t)$ reaches its peak before $\Omega_1(t)$, the eigenstate (4) matches the initial state of the system (state 1). Since, for long pulses, the system state adiabatically follows the state ψ_z, the occupation probability is transported from state 1 to state 3. Because state 2 is not involved in the eigenstate ψ_z, it is not populated during the pulse sequence.

The situation for the molecule is rather different because we have an extra degree of freedom: the molecular coordinate which we denote by R. With the Hamiltonian now given by Eq. (1), and the spatially varying potentials (2), it is clear that it is impossible in this molecular case to have the two-photon resonance condition used in the atomic case (except at isolated points). Thus there is no zero eigenstate in the molecular situation.

At this point it could be argued that rather than viewing the Hamiltonian (1) in the position basis, we should utilize a vibrational basis so that we could recover a version of the atomic STIRAP process seen with the Hamiltonian (3). However, while the vibrational picture and the spatial picture are entirely equivalent, we believe that the key to understanding the phenomenon in Fig. 2 is not the vibrational basis but a spatial picture. This brings us to a fundamental difference between STIRAP and the phenomena in this Letter. If we had a STIRAP process taking the system from the $X^1\Sigma_g^+$ ($\nu = 0$) vibrational state to the $2^1\Pi_g$ ($\nu'' = 0$) vibrational state we would see only the disappearance of the wave packet in Fig. 2(a) and its reappearance in Fig. 2(b) without the smooth positional shifting of the wave packet. The reason is that the $X^1\Sigma_g^+$ ($\nu = 0$) vibrational state wave function will be approximately the ground vibrational wave function of a harmonic oscillator, and any positional movement of the wave packet must be due to the excitation of other vibrational states. We can say the same thing about the $2^1\Pi_g$ ($\nu'' = 0$) vibrational state, i.e., that if only the ($\nu'' = 0$) were involved there would be no shifting of the wave packet as seen in Fig. 2(b). So the process of Fig. 2 is not direct STIRAP transfer between $X^1\Sigma_g^+$ and $2^1\Pi_g$.

Our explanation for the transfer of the wave packet in the manner seen in Fig. 2 relies on *light-induced potentials* [10]. For wave packets that travel sufficiently slowly through systems of coupled potential surfaces the nature of the field-dressed potential energy surfaces becomes more important than the bare (i.e., not coupled by light) energy surfaces. This means, for example, that

a laser-induced crossing becomes an avoided crossing with an energy gap which increases with the intensity of the laser. The energy gap can become large enough to allow the passage of a wave packet which would not otherwise penetrate the crossing; this leads to bond softening [11]. The eigenvalues of (2) determine the light-induced potentials, and in Fig. 3 we show the most relevant one as a function of space and time. The most striking feature is the kinked channel which is responsible for guiding the wave packet from one position to another.

At $t = 0$ the light-induced potential of Fig. 3 is composed of the $X^1\Sigma_g^+$ potential on the left hand side of the picture, and the $2^1\Pi_g$ potential on the right hand side of the picture. In effect there is a very small avoided crossing of these two potentials near $R = 3.4$ Å. The crossing is small because at $t = 0$ the two laser fields are very weak. As a result, there are two wells in the field-dressed state at $t = 0$, one belonging to the $X^1\Sigma_g^+$ state, where the initial wave packet resides, and the other belonging to the $2^1\Pi_g$ state, which is where we aim to transfer the wave packet. Because of the red detuning of the two pulses, the field-dressed state corresponding to the intermediate $A^1\Sigma_u^+$ state (at $t = 0$) lies well below the field-dressed potential of Fig. 3. However, as the pulse resonant with the $A^1\Sigma_u^+ \rightarrow 2^1\Pi_g$ transition turns on there is a repulsion between the A-type ($A^1\Sigma_u^+$ at $t = 0$) field-dressed state and the rhs of the field-dressed state in Fig. 3 (which is Π-like). This repulsion results in the disappearance of the rhs channel in Fig. 3. The repulsion also moves the A-Π avoided crossing to larger internuclear separations.
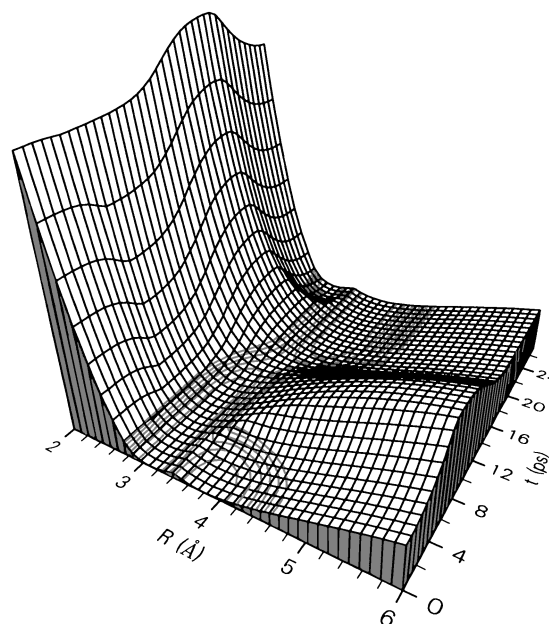

FIG. 3. Space and time dependence of the light-induced potential responsible for the transportation of the wave packet in Fig. 2.

When the second pulse is turning on, the repulsion between the X part of the state in Fig. 3 and the lower A state pushes the main channel upwards in energy and also displaces it to the right because the right hand part of the state in Fig. 3 has more of the Π character, and is not repelled from the A state by the second pulse. As the first pulse dies away the transfer of the wave packet completes with the approach of an avoided crossing from *small* internuclear separations. Eventually this avoided crossing becomes the same X-Π avoided crossing seen near $t = 0$, so we again have two wells in the potential.

It can be clearly seen from Fig. 3 that we need to have a counterintuitive sequence of pulses. Having an intuitive sequence would be like starting from the rear of Fig. 3 in the left hand well. But the left hand well is a dead end. Only the right hand well lies in the channel connecting the wave packet through the pulse sequence. Because the process is carried out slowly (adiabatically), the original wave packet can not only be transported from one space position to another, but can also change its shape at the same time. For example, if the Π state had a much narrower potential (high vibrational frequency) the same sequence of pulses could be carried out and the wave packet would be adiabatically squeezed as it moves along the light-induced channel into its final state.

The treatment presented here has been restricted to only three levels in the sodium dimer. There is always the possibility that other neighboring energy levels could disturb the counterintuitive process by complicating the dressed state potential seen in Fig. 3. This will be subject to further investigation. Fortunately, the scheme presented in this Letter is extremely insensitive to the specific parameters (Rabi frequency and detuning) once the appropriate regime has been discovered. Thus we expect that there is enough freedom in the controlling parameters to avoid any detrimental effects from other levels.

We have described a process for the efficient transfer of a wave packet from one molecular potential to another by means of light-induced potentials. We have demonstrated it with the sodium dimer using realistic pulse parameters and potentials. A suitable name for the process is adiabatic passage by light induced potentials (APLIP). The process is not only efficient, but usable over a wide range of counterintuitive pulse parameters. The range of parameters is even wider than in a corresponding STIRAP excitation because we do not maintain a precise two-photon resonance, and do not have the possibility of excitation of neighboring vibrational levels. The process can also be quite fast, almost on vibrational time scales.

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