Adiabatic passage by light-induced potentials in molecules

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We present the APLIP process (Adiabatic Passage by Light Induced Potentials) for the adiabatic transfer of a wave packet from one molecular potential to the displaced ground vibrational state of another. The process uses an intermediate state, which is only slightly populated, and a counterintuitive sequence of light pulses to couple the three molecular states. APLIP shares many features with STIRAP (stimulated Raman adiabatic passage), such as high efficiency and insensitivity to pulse parameters. However, in APLIP there is no two-photon resonance, and the main mechanism for the transport of the wave packet is a light-induced potential. The APLIP process appears to violate the Franck-Condon principle, because of the displacement of the wave packet, but does in fact take place on timescales which are at least a little longer than a vibrational timescale.

33.80.-b, 42.50.-p

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 timescales close to, but longer than the vibrational timescales.

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 $X^1\Sigma^+_g$ state, the $\Lambda^1\Sigma^+_u$ 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.

![Fig. 1. The three Na$_2$ potential energy surfaces used in our calculations: the $X^1\Sigma^+_g$ ground state, the $\Lambda^1\Sigma^+_u$ 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.](image-url)
\[
H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} I + \mathcal{U}(R, t)
\]
where \( R \) is the internuclear separation, \( m \) is the reduced mass of the molecule, and the electronic potentials and couplings are given by

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

Here \( U_X(R), U_A(R), \) and \( U_{\Pi}(R) \) are the three potentials, \( \delta_1 \) and \( \delta_2 \) are the detunings of the two pulses from the lowest points of the potentials, and \( \Omega_1(t) = \mu_X A E_1(t)/\hbar, \Omega_2(t) = \mu_A h E_2(t)/\hbar \) 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 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/cm²) 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 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 \( \Lambda \) 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 \( \Lambda \)-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

\[
H_a = \begin{bmatrix}
0 & \hbar \Omega_1(t) & 0 \\
\hbar \Omega_1(t) & \hbar \Delta & \hbar \Omega_2(t) \\
0 & \hbar \Omega_2(t) & 0
\end{bmatrix},
\]

where \( \Delta \) is the two-photon resonant laser-atom detuning, and \( \Omega_1 \) and \( \Omega_2 \) 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

\[
\psi_z(t) = \frac{1}{\sqrt{\Omega_1(t) + \Omega_2(t)}}[\Omega_2(t), 0, -\Omega_1(t)]^\top
\]  

(4)
to achieve the transfer directly from state 1 to state 3. We note that the state \(\psi_z\) 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 \(\psi_z\), the occupation probability is transported from state 1 to state 3. Because state 2 is not involved in the eigenstate \(\psi_z\), 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 co-ordinate 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, whilst 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 only see 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 comprised of the \(X^1\Sigma_g^+\) potential on the left hand side of the picture, and of 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 \(A^1\Sigma_u^+\) state at \(t = 0\) field-dressed state and the rhs of the field-dressed state in Fig. 3 (which is \(\Pi\)-like). This repulsion results in the disappearance of the rhs channel in Fig. 3. The repulsion also moves the \(A^1\Pi\) avoided crossing to larger internuclear separations.
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 also displaces it to the right because the right hand part A state pushes the main channel upwards in energy and between the X part of the state in Fig. 3 and the lower t

crossing becomes the same X-Π avoided crossing seen

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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 pro-
cess 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 corre-
sponding STIRAP excitation because we do not maintain

a precise two-photon resonance, and do not have the pos-
sibility of excitation of neighbouring vibrational levels.
The process can also be quite fast, almost on vibrational
timescales.

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[8] We neglect spontaneous emission in this Letter, though it can be included in the numerical treatment (see Ref. [2]). For short interaction times the influence of spontaneous emission is small, partly because the intermediate state is not populated during the process.


