Vibrationally-induced electronic population inversion with strong femtosecond pulses

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We discover a new mechanism of electronic population inversion using strong femtosecond pulses, where the transfer is mediated by vibrational motion on a light-induced potential. The process can be achieved with a single pulse tuning its frequency to the red of the Franck-Condon window. We show the determinant role that the sign of the slope of the transition dipole moment can play on the dynamics, and extend the method to multiphoton processes with odd number of pulses. As an example, we show how the scheme can be applied to population inversion in Na$_2$.

The development of femtosecond pulse technology has allowed the first experimental observation of transition structures that are fundamental to study chemical reactivity and kinetics\[1\]; ultrafast imaging and structural dynamics are currently providing a wealth of spectroscopic and structural information concerning the dynamics of molecules in real time\[2, 3\]. Additionally, as the laser acts on the time scale of the nuclear dynamics, ultrafast and strong pulses can be used not only to monitor but also to control the movement of atoms, modifying the yield and rate of chemical reactions\[4, 5\]. The use of closed-loop learning techniques has allowed a fast fully experimental approach to control quantum processes in molecules with strong fields\[6, 7\]. However, the experimental observation alone is often not enough to rationalize the outcome of the experiments. In many cases, understanding the underlying processes requires the use of models and theoretical simulations to describe the key aspects of the dynamics. This is the approach followed in this work.

To maximize the transition probability between two quantum states coupled by an external field is the fundamental challenge underlying most quantum control schemes. When the interaction is coherent, it is possible to achieve full population inversion through Rabi flopping by controlling the pulse area\[8, 9\]. In molecules, however, the density of states forces the use of very long pulses, which make energy relaxation and decoherence a major concern. Using shorter (and hence stronger) pulses renders a new problem due to the Autler-Townes splitting generated by the accessible yet unpopulated vibrational levels in the ground state\[10, 11\]. This can be beaten by working with very short pulses, demanding even stronger pulses\[12\].

Under strong fields, a plethora of new phenomena occur in molecules. Aside from ionization or other multiphoton processes, the potential energy surfaces change due to dynamic Stark shifts, dramatically affecting the resonances and photophysics of the molecule\[13, 14\]. One can modulate these laser-induced potential energy surfaces (LIPs) as drivers of the dynamics\[15\]. Several photodissociation reactions were controlled in such way, where under certain conditions the number of photons is conserved, that is, the laser acts as a catalyst\[17, 19\].

On the other hand, population inversion is typically controlled by chirping the laser, with the frequency of the pulse sweeping across the absorption band, although by modulating the field the pulse duration is stretched\[20, 22\]. It is possible however to achieve adiabatic passage with transformed-limited pulses, as in the APLIP (adiabatic passage by light-induced potentials) scheme\[24, 25\]. Several APLIP scenarios have been proposed\[26–28\], but all of them require the use of at least two time-delayed pulses non-resonantly coupled to an intermediate state. The key of the method lies in the presence of this intermediate electronic state that assists in modulating the LIP to guide the wave packet motion from one electronic state to the other.

If the pulses are long enough, this “motion” is in fact adiabatic or quasi-static, by which the wave packet always remains at the bottom of the LIP preserving the initial vibrational quanta\[26, 28\]. However, less-adiabatic or ultrafast APLIP are also possible\[12\]. In addition, it has been proven that the APLIP principle can be extended to work for any system with an odd number of potentials (N), simply by using N – 1 pulses\[29\]. While in this case the method maintains its robustness against changes in the field and its vibrational state selectivity, the intermediate electronic states are populated transiently during the process, in contrast to APLIP.

In this work we want to demonstrate that a similar effect can be achieved using a single pulse that couples two electronic states slightly off-resonance. In this case the electric field will induce a different Stark effect on two different parts of the potential energy surface, creating an effective LIP that will allow the system to oscillate between the two coupled states. This asymmetry in the Stark effect can be provoked by an antisymmetric (with respect to the internuclear distance) transition dipole too. However, the transition cannot be adiabatic in the nuclear motion. If the pulse is switched on slowly (its ramp up quite larger than the period of vibrational motion) then the wave packet will adiabatically shift from the equilibrium geometry at $V_1$ to that at $V_2$, only to revert the transition when the pulse is switched off. The
control mechanism that we propose in this work relies on the correlation between the vibrational motion and the electronic state for which we term the scheme the Vibrationally Induced Electronic Transition in a Light-Induced Potential or VIETLIP.

Fig. 1 reveals such effect for the simplest system formed by two harmonic oscillators, $V_1$ and $V_2$, coupled by a field. For illustration purposes we have chosen the reduced mass of the system to be that of Na$_2$ and the fundamental harmonic frequency $\omega$ to roughly correspond to that of its ground electronic state. The origin of the internuclear distance is chosen in between the equilibrium geometries of both potentials. In the first case [Fig.1(a)] we choose the excited state to be exactly as the ground state but shifted to a new equilibrium geometry, $R_1 - R_0 = \delta$, where $\delta = 2a_0$ (approximately the displacement of the equilibrium geometries of the ground and first excited electronic states of Na$_2$). We assume a constant transition dipole. Because we are not exciting at the Franck-Condon region, the transition from $V_1$ to $V_2$ is hindered by an energy barrier $V_0$ that the nuclear wave packet, initially in $V_1$, must overcome.

A strong field generates LIPs, $U_1$ and $U_2$: $U_1$ correlates with $V_1$ at short $R$ and with $V_2$ at large $R$. Since it does not have any internal barrier, a nuclear wave packet initially prepared in $U_1$ will freely move from $V_1$ to $V_2$. $U_2$ shows the opposite correlation. Fig. 2(a) shows the electronic population in $V_2$ at the end of the excitation as a function of the pulse duration (plateau of the pulse), obtained after integrating the time-dependent Schrödinger equation in a grid [30] in the rotating wave approximation (RWA) [32]. We use plateau pulses with a relatively fast sine square switch on/off of 60 fs and a plateau of duration $\tau$. The electronic population follows a slow squared-type oscillation with a period that depends on the period of motion of the nuclear wave packet in the LIP. The period depends weakly on the pulse amplitude because the curvature of the LIP (and hence the harmonic frequency) depends on the strength of the coupling. For weaker pulses the period will be larger. In any case the period is of the order of hundreds of femtoseconds, an order of magnitude (or more) larger than the Rabi period which depends on the pulse amplitude. For strong pulses the Rabi frequency is comparable to an electronic transition energy.

The VIETLIP scheme works as long as the equilibrium geometries of the electronic potentials $V_1$ and $V_2$ are separated enough, but if $\delta$ is too large, $E_0$ will be large too, and the scheme will require very strong pulses to remove the energy barrier in the LIP. On the other hand, if $\delta$ is smaller than the de Broglie wavelength of the initial nuclear wave function, then part of this wave function correlates with $U_1$ in the adiabatic representation (for $R < 0$), and part of it with $U_2$ (for $R > 0$), as shown in Fig. 1(b). Under a strong field we generate a wave packet in two LIPs with no internal barriers, leading to interference and electronic beatings. An example is shown in Fig. 2(b) where we use the same potentials as before but with $\delta = a_0$. The population fully oscillates at a Rabi period that depends exclusively on the Rabi frequency.
For strong fields this implies electronic beatings in the order of the femtosecond.

However, it is interesting to see that the presence of a coordinate-dependent transition dipole can compensate this effect. In Fig.1(b) we show the LIPs when $\delta = 1\lambda_0$ but the dipole depends linearly with the internuclear distance, $\mu = R$. The effect of the dipole is to separate the equilibrium geometries of the LIPs, allowing to prepare the initial wave function in a single LIP. The slope of the dipole (positive or negative) decides the the shape of the LIPs. If the coupling is $-R \times \epsilon$ (positive slope; larger dipole at large $R$) where $\epsilon$ is the field, then, as in Fig.1(b) $U_1$ moves the wave packet towards $V_2$. The dynamics is relatively similar (although more complex) to that encountered in the first case. The oscillations in the yield as a function of the pulse duration show a long period corresponding to the nuclear motion, not to the Rabi oscillation. However, if the coupling is $R \times \epsilon$ (negative slope; larger dipole at small $R$) then the equilibrium geometry of $U_1$ is at $V_1$. The wave packet is relatively trapped at the ground electronic state, the trapping increasing with the pulse intensity. The yield of absorption is therefore quite smaller, as shown in Fig.2(c) and the absorption bands anti-correlate with those obtained with opposite dipole.

One of the most interesting aspects of population transfer through diabatic wave packet motion on a LIP is that the method can be extended to multiphoton transitions, but only with an odd number of pulses, contrary to the APLIP scheme, which works with an even number of pulses. Moreover the passage depends on the choice of the laser frequencies: for some arrangements the passage is more protected than for others. In Fig.3 we show the results of population transfer between 4 potentials, $V_1$ to $V_4$, where we assume that there are only sequential couplings between nearest neighbors so that $V_1$ is coupled to $V_2$ by $\Omega_1(t)$, $V_2$ with $V_3$ by $\Omega_2(t)$ and $V_3$ with $V_4$ by $\Omega_3(t)$. As in multiphoton APLIP, the intermediate potentials must be off-resonance. In our model we choose $V_2$ and $V_3$ as harmonic oscillators centered at the equilibrium geometries of $V_1$ and $V_4$ respectively, although the results are not very sensitive to these parameters. However, they are sensitive with respect to the choice of detuning: $V_2$ and $V_3$ are displaced $\pm \Delta$ in the vertical axis. For the results in Fig.3 we fixed the peak Rabi frequency as 0.05 a.u. and $\Delta = 0.08$ a.u. When $V_2$ and $V_3$ are above $V_1$ and $V_4$ (red detuning) full population transfer by VIETLIP is possible. The results are worse in the blue-detuning configuration ($V_2$ and $V_3$ below $V_1$ and $V_4$) since the Stark effect shifts the $V_1$ and $V_4$ potentials to higher energies. Robust population transfer is still possible, particularly with stronger fields. However, in the alternate configuration (when one potential lies above and the other below $V_1$ and $V_4$) the passage is clearly worse and less robust. In principle, the same ideas can be generalized to any multiphoton transition with odd number of pulses.

Although the concept of LIPs is essential in understanding many processes under strong fields, it has been experimentally difficult to show evidence of wave packet transfer through LIPs. One of the main difficulties for APLIP is to isolate the desired process from other competing routes. As more pulses act on the system the RWA is typically violated breaking the theoretical requirements for the transfer. Here we show that the VIETLIP scheme can be applied in realistic conditions. As an example, we show simulations for the dynamics in Na$_2$. We use ab initio electronic potentials and dipoles for the transition between the ground state $^1\Sigma_g(3s)$ and the first excited state $^1\Sigma_u(3p)$ that gives rise to the $A$ band.
Interestingly, the transition dipole is approximately linear in the internuclear distance and has the appropriate sign. Choosing the frequency at the Franck-Condon window (with maximal overlap with the vibrational levels in A) leads to saturation\cite{[11]}. However, if we tune the laser below the resonance ($\omega = 1.8$ eV) we obtain the results shown in Fig.4(a). Here we use Gaussian pulses of different peak amplitudes and pulse durations. We observe square oscillations with long periods that partially reproduce the behavior observed in Fig.2(a), although with quite lower pulse intensities (because of the large transition dipole).

The dependence of the yield on the pulse duration again basically follows from the vibrational motion of the wave packet in the LIP. Fig.5 shows the time evolution of the square of the wave packet for two pulse durations: 75 fs (within the maximum absorption band) and 150 fs (within the transparent conditions) using a pulse of $2.7 \times 10^{-3}$ GV/cm peak amplitude. If the wave packet has time to move from $V_1$ to $V_2$ through the LIP (first oscillation) we have maximum absorption. Doubling the time the wave packet returns to that part of the LIP that correlates to $V_1$ as the pulse is switched off.

Comparing the yield of absorption in Na$_2$ with the model results of Fig.2(a) shows some differences. A striking difference is the decay of the second band of maximum absorption (particularly with stronger fields) and the weak dependence of the position of the bands on the pulse amplitude. This is an effect due to the dipole. As observed in Fig.1(b) and Fig.2(c) the coordinate dependent dipole deforms the LIPs affecting the diabatic motion of the wave packet in the LIP, which is mostly trapped around the equilibrium geometry of the LIP for large fields (because the $R\epsilon$ term increases with the distance). For constant dipoles we fully recover the regular behavior, as shown in Fig.4(b). The simulations in this case where performed in the Na$_2$ potentials with an average constant dipole of 3.65 ea$_0$. Although the dynamics in the real Na$_2$ (with coordinate-dependent dipole) are more complex, the dipole in fact makes population inversion more robust, as evidenced by comparing the size of the absorption band as a function of the pulse duration in both cases.

In summary, we have proposed a new robust scheme of population inversion between two electronic states with displaced equilibrium geometries. The scheme shares many features with APLIP, as the mechanism of population transfer is mediated by motion in a LIP. In VI-ETLIP, however, only one strong pulse is needed, that must be tuned to the red of the absorption band, and shorter pulses can be used. The process cannot be completed in a fully adiabatic way, so that the pulse duration must be approximately synchronized to the vibrational period. Moreover the scheme can be extended to any multiphoton process with odd number of pulses. Finally, we have found an intriguing dependence to the dipole function. Obviously, a dipole going to zero for some internuclear distance has always strong implications in adiabatic passage\cite{[31]}. In this work we report for the first time how the sign of its slope determines the outcome of the transition, placing the molecular complexity in the forefront of the control process.

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