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Adiabatic and diabatic transformations as physical resources for wave packet squeezing

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We propose a scheme for squeezing vibrational wave packets in the ground (or excited) states of diatomic molecules that uses pulse sequences of strong nonresonant short pulses. The physical mechanism of the scheme is a two step process involving adiabatic and diabatic transformations of the wave packet. The first step is the adiabatic stretching of the wave packet on a light-induced potential, and the second step is dynamic squeezing by free evolution after ultrashort (i.e., diabatic) population transfer. We show that this sequence of transformations can be performed very efficiently with a simple two pulse sequence with slow switch on and fast switch off pulse shapes, and we analyze the required physical resources that are needed. We test the scheme on a model of harmonic oscillators and on the Rb_2 dimer. Finally, different possible generalizations are proposed.

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I. INTRODUCTION

Laser pulses are powerful and flexible tools that can be used to manipulate the properties of molecules [1,2]. Typically, the main physical resources are already in the (parent) transform-limited pulse: the pulse bandwidth, and intensity. Given a fixed bandwidth and peak amplitude, optimal phase and amplitude modulation leads to maximal use of the resources in the pulse in order to optimize the yield of the desired physical process [3–5].

The most successful quantum dynamics typically displays extended coherences and interferences in coordinate or state space, adequately controlled by time delays induced by the phase modulation, so that the "natural" Hamiltonian dynamics of the wave function cooperates with the desired motion. The quantum dynamics is codified in the optimal pulse parameters [5], but since the Hamiltonian and the pulse effects are all entangled in the dynamics, it is difficult to understand the underlying mechanism [6,7] and analyze what are the required physical resources and what are the limiting yields achievable, except for some idealistic cases where controllability theorems [8] can be applied. There are other ways of controlling the dynamics that make less extensive use of the pulse resources but which provide excellent results, especially in simpler systems, and allow a clear understanding of the role of the different pulse features.

In this paper we analyze vibrational wave-packet squeezing in diatomic molecules [9–16]. The convolution of the Hamiltonian-free dynamics and the laser coupling (the pulse shape) explain the squeezing dynamics in first-order perturbation, which is used in many schemes for focusing or squeezing on a excited potential, as analogues of light-squeezing in quantum optics [9,10,13,14]. The problem was also treated using optimal control techniques [15,16]. By phase modulation of the pulses, optimal squeezing on excited potentials was observed to involve interference between the head and tail of the wave packet or between two wave packets promoted at different times. In Na_2, up to 50% squeezing was achieved [16]. Recently, other physically motivated schemes were proposed.

In this paper we are interested in control strategies that clearly unravel or distinguish three different processes in the dynamics: diabatic transformations of the wave packet between electronic states, which preserve its shape, free motion on the electronic potential, which preserves the energy, and adiabatic transformations of the wave packet between electronic states, which preserve the eigenstate populations, i.e., the structure. The first ones are the typical "vertical" Franck-Condon excitations, which rely essentially on the bandwidth of the pulses. The second ones are "horizontal" laser-free displacements, which may change the shape of the wave function, among other interesting quantum effects. Finally, the third ones involve "diagonal" excitation of the wave packet, whose shape adapts to the topology of the potential, which is itself modulated by the laser pulses [17–19]. The target potential can be either an electronic excited state of the molecule [20–22], or an artificial laser-controlled light-induced potential (LIP) [23–25]. The adiabatic transitions demand essentially intensity resources on the pulses. The pulse resources needed to optimally operate in each process are clearly identified in these strategies, so that a physically motivated choice of mechanism can be performed.

We have previously used both adiabatic dynamics and diabatic transformations to squeeze wave packets. The adiabatic squeezing (AS) scheme [27] allowed the freezing of the squeezed wave packet so that the dynamic dephasing could be experimentally controlled. However, this achievement implied high intensity laser resources and small squeezing could be gained. The iterative stretching-squeezing (ISS) scheme [28], on the other hand, just required pump-dump control with ultrashort laser pulses [29,30], but it relied heavily on the "natural" squeezing dynamics of a free-evolving wave packet, which is hampered in anharmonic re-

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*Author to whom correspondence should be addressed. Electronic address: ignacio@tchiko.quim.ucm.es gions of the potential. However, for a clever choice of molecule and electronic state one could easily achieve 50% squeezing. In this paper we propose another method, that uses both adiabatic and dynamic squeezing resources with the goal of reducing both the time and intensity demands of the AS scheme, and the bandwidth demands of the ISS scheme. We call this mechanism the adiabatic-diabatic squeezing (ADS) scheme. In this work we apply the ADS scheme to both ideal systems (harmonic oscillators) and realistic molecules, showing that the achieved squeezing is typically as good as in the ISS scheme, and that it can be applied in more general cases.

II. THE PRINCIPLES OF THE SCHEME

In order to understand the general principles of the ADS scheme and its connection with adiabatic and iterative dynamic squeezing, we would like first to analyze in a very broad way how the different schemes operate, what transformations they use and how these transformations can be relaxed or generalized.

The mechanism of the AS scheme [27] can be summarized in the one-step process

$$V_1(x) \xrightarrow{\text{squeeze}} U_n(V_1, \ldots, V_{n+1}), \tag{1}$$

where $U_n(V_1, \ldots, V_{n+1})$ is a LIP narrower than the original potential that is prepared and controlled by a n pulse adiabatic sequence $\{\Omega_j(t)\}$. Unless the molecule has excited electronic configurations tighter than the ground state, the adiabatic squeezing will at least require two photon preparation of the LIP, but we will regard these two or n-pulse adiabatic sequences as a single transformation of the wave packet. The "final" n-pulse parameters $\{\Omega_j\}$ can be chosen so that $U_n(V_1, \ldots, V_{n+1})$ is maximally narrow, that is, one can perform an static optimization of the LIP. Additionally, one has to find the adiabatic path that connects the initial wave function to the desired LIP. The adiabatic process assures a quasistatic excitation of the wave packet, that will remain "frozen" on the target configuration, but it demands strong conditions on the pulse amplitudes and durations. However, the adiabatic conditions can be relaxed. Shorter and less intense pulse sequences can drive all the electronic population to the desired LIP without allowing full reshaping of the wave packet along the process. Then the wave packet will no longer be stationary on the LIP. Even if the LIP is highly anharmonic, initially the free motion on the potential implies the breathing of the packet's width leading to further dynamic squeezing beyond that obtained at the maximally squeezed equilibrium configuration. By relaxing the adiabatic conditions and in particular the time duration of the pulses, one moves from the adiabatic to the diabatic regime, but the representation based on light-induced potentials is only fruitful as long as all the population remains in a single LIP. A minimum time duration for the pulses is needed to move the wave packet, that will depend on how far the equilibrium configuration of the LIP is with respect to the initial configuration, setting the time limits of the adiabatic scheme.

The ISS approach to squeezing uses a sequence of diabatic transformations time-delayed by free motion of the wave packet on the potentials [28], which can be described by the cyclic two-step procedure

$$\begin{aligned} V_1(x) &\xrightarrow{\text{stretch}} V_2(x) \xrightarrow{\text{squeeze}} V_1(x) \cdots \\ &\xrightarrow{n \text{ stretch}} V_2(x) \xrightarrow{n \text{ squeeze}} V_1(x), \end{aligned} \tag{2}$$

where the two transitions are diabatic (fast vertical Franck-Condon excitation). If the binding well in $V_2(x)$ is more relaxed than in $V_1(x)$, the scheme leads to dynamic stretching in $V_2(x)$ and dynamic squeezing in $V_1(x)$, which increases at each iteration. In principle both transitions could be multiphoton, but the key principle of the scheme is the time separation of the transitions, as opposed to the single multiphoton transformation performed in the AS scheme. The ISS scheme allows more squeezing of the wave packet after many iterations, at the expense of large bandwidth transform limited pulses.

A good compromise between both previous schemes is obtained when the iterative sequence is replaced by a two-step process

$$V_1(x) \xrightarrow{\text{stretch}} U_w(V_1, \ldots, V_{n+1}) \xrightarrow{\text{squeeze}} V_j(x), \tag{3}$$

where the first step implies maximally stretching the wave packet under adiabatic guidance, that is, a LIP is prepared by mixing $n+1$ electronic states (with may include dissociative states) using n pulses with maximum width. In a sense the underlying idea is to replace the n diabatic steps leading to dynamic stretching for a single n photon optimization of the LIP. The second step is a m pulse diabatic "reversion" of the first transformation, driving all the population to a potential $V_j(x)$ that belongs to the LIP mixture, and typically is $V_1(x)$, so that the evolving wave packet leads to dynamic squeezing on a single potential. This is the mechanism of the ADS scheme. A simple sketch of it is depicted on Fig. 1, where we show snapshots of the wave packet on the adiabatic and diabatic frame at important times of the process. The data shown in Fig. 1 actually corresponds to one example for the Rb_2 molecule, which is later explained in the text.

From the static point of view, the best performance is achieved when the first step involves optimal adiabatic stretching, as opposed to the optimal adiabatic squeezing in AS [27]. By optimal adiabatic stretching one can typically obtain very wide wave packets near the dissociation limit [23,24,26]. However, several constraints should be imposed to this optimization because reverting the wave packet diabatically can be difficult, and moreover the dynamics in regions of high anharmonicity can lead to strong dispersive effects that stop the breathing motion. The static optimization should balance the need for a wide wave packet sitting not too far from the potential $V_j(x)$, where the population will be transferred during the fast diabatic transformation. Again, the adiabatic demands of the first transformation can be relaxed so as to gain some additional dynamic stretching of the wave packet.

In this paper we will consider probably one of the simplest and most useful scenarios, where three electronic states are coupled by two lasers. A simple adiabatic sequence con-

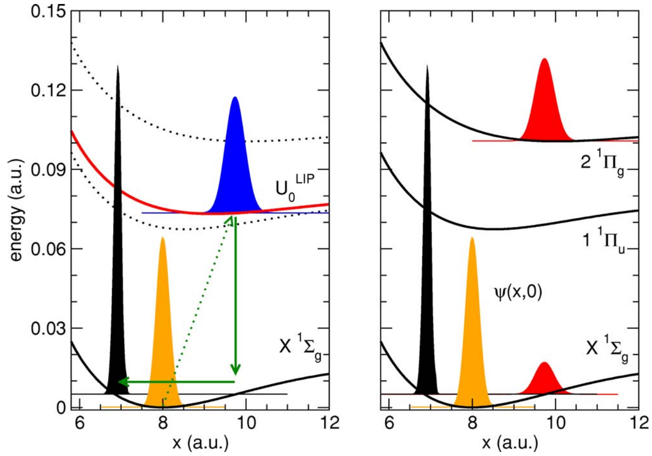

FIG. 1. (Color online) Wave packet dynamics in the ADS scheme, followed in the adiabatic (a) and the diabatic representation (b). The arrows in the graph show the three stages of the process; adiabatic pump leading to stretching, ultrafast (diabatic) dump, and free evolution leading to squeezing. The two wave packets in the ground and excited potentials correspond to the adiabatic wave packet in the LIP U_0. The example corresponds to maximal squeezing in Rb_2.

trolling the time-delay and the frequency shift from resonance is enough to displace and shape the wave packet on a wide LIP. In this scenario, the second step just requires a fast switching off of the pulses in a given order. An even simpler scenario is possible. The ADS scheme can be implemented such that U_w is in fact a single (wide) electronic potential of the molecule, so that the first step requires the adiabatic excitation of the ground state of the relaxed electronic configuration using a single chirped pulse, and the second step is a "vertical" Franck-Condon transition back to the initial potential. However, a single pulse typically does not allow very efficient squeezing. Either the squeezing is small or the adiabatic and diabatic transformations are very hard to accomplish with high population transfer. For that reason we will only consider the two-pulse, three electronic states case.

III. DIFFERENT IMPLEMENTATIONS OF THE ADIABATIC-DIABATIC SCHEME

As an illustration of the ADS scheme and the different possible implementations that it enables, we consider in this section a model system using three symmetrically displaced harmonic oscillators [31] (SDHO). Following the typical convention for the adiabatic states, the three formed LIPs are labeled $U_+(x,t)$, $U_0(x,t)$, and $U_-(x,t)$ in order of decreasing energy.

Although mathematically too simple to account for all the dynamic effects on molecules, the SDHO poses an extraordinary challenge for wave-packet squeezing. In the adiabatic squeezing scheme one can use two possible pulse sequences in order to prepare narrow LIPs, red-detuned counterintuitive sequences (C,r) [preparing $U_0(x,t)$], or blue-detuned intuitive sequences (I,b) [preparing $U_+(x,t)$]. The LIPs, formed by the inner wall of the excited potential $V_3(x)$ and the outer wall of the ground potential $V_1(x)$, allow around 25% squeezing of the packet's width [27] using quite strong pulses. On the other hand, since for all three potentials the harmonic frequency is the same (so that the ratio of frequencies γ, is equal to 1), the ISS scheme [28] will not provide dynamic squeezing by coupling any of the harmonic oscillators.

For the ADS scheme we first need to prepare a wide LIP. Again two adiabatic sequences allow this process. A blue-detuned counterintuitive sequence (C,b) prepares a wide $U_0(x,t)$, and a red-detuned intuitive sequence (I,r) creates $U_-(x,t)$. These are the LIPs that allow the simplest adiabatic passage to the excited state, since the initial potential correlates naturally with the LIP without needing too strong pulses [21,27]. For the SDHO model, the optimal pulse parameters are symmetric ($\Omega_1=\Omega_2$, $\Delta_1=\Delta_2$) leading to wider LIPs sitting right at the intermediate separation between $V_1(x)$ and $V_3(x)$, where both electronic potentials are equally populated [27]. The width of the LIP decreases with the Rabi frequency but a minimum pulse intensity is required, since for weak pulses the LIP (and the wave packet) splits into a double well structure [26]. Depending on the choice of pulse sequence at the switch-off process, and on simple deformations of the switch-on step, we consider three possible implementations.

For the following numerical results, we have solved the time-dependent Schrödinger equation in the rotating-wave approximation

$$\frac{\partial}{\partial t}\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\end{pmatrix} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\mathcal{I} + \begin{pmatrix} V_1(x)-\Delta_1 & -\Omega_1(t)/2 & 0\\ -\Omega_1(t)/2 & V_2(x) & -\Omega_2(t)/2\\ 0 & -\Omega_2(t)/2 & V_3(x)-\Delta_2 \end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\end{pmatrix}, \tag{4}$$

where the Rabi frequencies $\Omega_j(t)=\mu_j(x)\mathcal{E}(t)$ are parametrized as a three step function with switch on $\Omega_j(t)=\Omega_j\sin^2(\pi t/2\tau_{1j})$ between $0\leqslant t<\tau_{1j}$; plateau $\Omega_j(t)=\Omega_j$ between $\tau_{1j}\leqslant t<\tau_{2j}$; and switch off $\Omega_j(t)=\Omega_j\cos^2(\pi(t-\tau_{2j})/2\tau_{3j})$ between $\tau_{2j}\leqslant t<\tau_{3j}$. Here and for the rest of the paper we have assumed constant transition dipole moments (Condon limit).

A. Case 1

In this section we consider the typical implementation, following closely the procedure explained in Sec. II: We first prepare a wide LIP by the counterintuitive blue-detuned (C,b) or the intuitive red-detuned (I,r) sequence and quickly switch off the pulses following the reversed sequence, so that the population is back-transferred to the ground state $V_1(x)$, where dynamic evolution will squeeze the wave packet.

For the (C,b) case the LIP is $U_0(x,t)$ and the reverse diabatic process implies first switching off $\Omega_1(t)$ and then $\Omega_2(t)$. The minimum Rabi frequency that guarantees squeezing in the LIPs is approximately 0.015 a.u., where the popu-

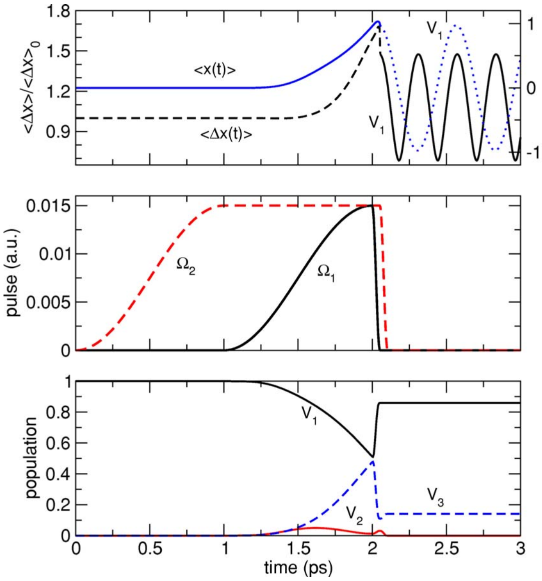

FIG. 2. (Color online) Dynamics of the ADS scheme (C,b) with reversed switch off sequence, for the HO model. The initial wave function is first stretched in $U_0(x,t)$ and then squeezed back in $V_1(x)$, where the wave packet is breathing. In the upper frame we show the width of the wave packet (left scale) and the average position (right scale). Also shown are the pulse shapes and electronic populations.

lations of $V_1(x)$ and $V_3(x)$ are approximately 50%. For the (I,r) case the wide LIP is $U_-(x,t)$ and the diabatic transformation requires first switching off $\Omega_2(t)$ and then $\Omega_1(t)$. The minimum necessary Rabi frequency is 0.013 a.u. where the electronic populations are about 40% in $V_1(x)$ and 30% in both $V_2(x)$ and $V_3(x)$.

In Fig. 2 we show the dynamics for the (C,b) case. A quite similar dynamics is observed in the (I,r) case. The pulses are chosen so that the switch on is slow ($\tau_{1j}=1$ ps) and the switch off is fast ($\tau_{3j}=50$ fs). The plateau region is 1.05 ps for the pulse that starts and ends the pulse sequence (for the other pulse there is no plateau). The relatively slow switch on and fast switch off guarantees that more than 90% of the population is first pumped into the LIP and then dumped to $V_1(x)$ in the diabatic transition. In fact, τ_1 is not large enough to assure full adiabatic freezing of the packet in the wider LIP, and it accounts for some small additional dynamic stretching, which is finally transformed into additional squeezing. A faster switch on can be used allowing more squeezing, but with greater losses in the final population in $V_1(x)$, while a slower switch off allows full population transfer at the expense of losing some small degree of squeezing. The switch on can be done even in 80 fs (and the switch off in around 10 fs) so that the whole adiabatic part becomes almost fully diabatic. However, this is at the expense of around 40% population loss in $V_1(x)$ at the final time.

Since the potentials are harmonic oscillators, the period of breathing is twice the period of oscillation and there is no distortion due to anharmonicity. Some small deviations can however be observed, since the LIP is not harmonic and hence the starting wave packet after the diabatic transition may not be exactly Gaussian. The final achieved maximum squeezings are 32% and 35% for the (C,b) and (I,r) schemes, respectively.

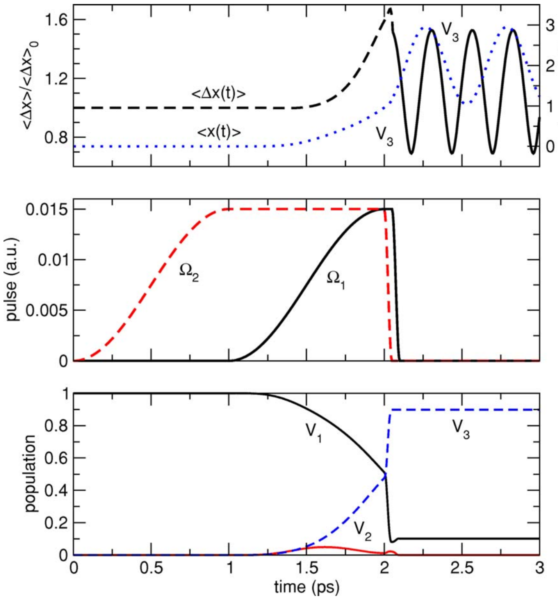

FIG. 3. (Color online) Dynamics of the ADS scheme (C,b) with the same switch off order, for the HO model. The initial wave function is first stretched in $U_0(x,t)$ and then transferred and squeezed in $V_3(x)$, where the wave packet is breathing. In the upper frame we show the width of the wave packet (left scale) and the average position (right scale). Also shown are the pulse shapes and electronic populations.

B. Case 2

It suffices to make a simple change in the pulse sequence at the switch off process to change the potential to which the population is transferred. For instance, in Fig. 3, we first switch off $\Omega_2(t)$ and then $\Omega_1(t)$ to diabatically transfer the population from the LIP to $V_3(x)$, using the (C,b) sequence. In fact, this is the typical adiabatic passage sequence. In this case, since the SDHO model is symmetric, the same dynamics occurs in comparison with Fig. 2. The same procedure could be used in the (I,r) sequence.

In typical molecules, $V_3(x)$ will be wider than $V_1(x)$ so that this implementation will lead to smaller final squeezing, since the amplitude of the breathing depends on the relative width of the initial wave packet with respect to that of the potential. However, if the wider LIP has a large component of $V_3(x)$ and therefore the average position is presumably very displaced from the ground electronic state configuration, then the diabatic transition to $V_1(x)$ will be difficult and will require more time, allowing for some reshaping of the wave packet (reducing its width) along the way. More importantly, only for harmonic potentials is the width of the parent LIP the only parameter that controls the final squeezing. In realistic potentials the anharmonicity of the system can dramatically reduce the squeezing, or even increase the dispersion of the originally wide wave packet. For this reason it may be convenient to diabatically transfer the popula-

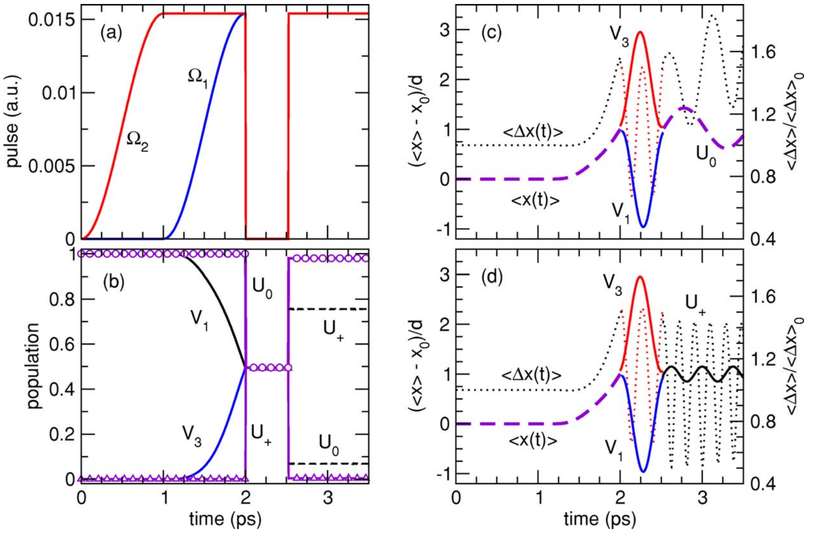

FIG. 4. (Color online) Adiabatic-diabatic releasing and retrapping dynamics in the HO model. In (a) we show the pulse profiles, where both pulses fully overlap at final times. In (b) we show the electronic and LIP populations. Lines with symbols refer to the case where the relative phase between the pulses is $\varphi=0$ and the dashed lines refer to $\varphi=\pi$. In (c) and (d) we show the average position (left scale) and width of the wave packet for $\varphi=0$ and $\varphi=\pi$, respectively. First the wave packet moves to the equilibrium configuration of $U_0(x)$ and stretches. At intermediate times the pulses are off and the adiabatic wave packet splits into ψ_1, moving in $V_1(x)$ to lower bond distances, and ψ_3, moving in $V_3(x)$ to larger bond distances. Finally the wave packets recombine moving either to $U_0(x)$ or to $U_+(x)$.

tion to the closer $V_3(x)$ potential. In this case the squeezing will only occur if the LIP is wider than $V_3(x)$, as in the SDHO model. For very wide $V_3(x)$ potentials the LIP will likely be narrower than the excited state.

The properties of the SDHO model allow for greater possibilities in the control of the dynamics. For instance, it is possible to adiabatically trap the wave packet in the LIP, and release it again diabatically whenever it is convenient. This allows one to control the time at which one wants to obtain the squeezed wave packet, since the wave packet does not dephase while it is adiabatically frozen in the LIP. It is also possible to change the diabatic sequence so that the population is split into both $V_1(x)$ and $V_3(x)$, just by switching off simultaneously both pulses. In Fig. 4 we show two possible implementations of the trapping-releasing dynamics, where the population is left to evolve freely during one cycle in both $V_1(x)$ and $V_3(x)$ before trapping it again in the LIP. Initially the population is in $U_0(x,t)$. The fast and simultaneous switch off splits 50% of the population to $V_1(x)$ and $V_3(x)$ which evolve from the Franck-Condon window at the crossing of both potentials. Finally, the fast switch on at the time at which the wave packets reencounter in the Franck-Condon window, reassembles the LIP again. All the population is then back in $U_0(x)$, although in the example shown in Fig. 4(c) the adiabatic wave packet is oscillating in the LIP. This retrapping process is sensitive to the relative phase of the pulses. For instance, if we apply a π phase shift to one of the pulses, then the wave packet will be trapped in $U_+(x)$, which is a narrow potential (it is used in adiabatic squeezing [27]). As Fig. 4(d) shows, the retrapping in $U_+(x)$ leads to greater ($\sim 50\%$) squeezing because the initially wide wave packet is breathing in the narrow LIP, whereas the anharmonic motion of the wave packet in $U_0(x)$ causes some spreading of the wave packet. However, there is some higher loss of population transfer in going to $U_+(x)$.

The protocol of diabatic releasing the LIP, free motion, and diabatic retrapping can be used to switch diabatically from one LIP to another, at least in this simple example [32]. Although many of these adiabatic-diabatic cyclic transformations are unlikely to be useful in realistic molecules, at least after several vibrational periods, they show some remarkable properties that perhaps could find greater utility in different physical systems [25].

C. Case 3

In this case we consider a different way of inducing nonadiabatic effects on the adiabatic transition, that leads to motion in the LIP and additional dynamic stretching and squeezing. Consider again the (C,b) sequence. $\Omega_2(t)$ is first switched on with $\tau_1=1$ ps, but if the second pulse $\Omega_1(t)$, is switched on more quickly ($\tau_1=250$ fs), it can reach the plateau value before $\Omega_2(t)$. Then all of the population will remain in $U_0(x,t)$ but the wave packet will oscillate and breathe in the LIP. We can wait until the width is maximum and then perform the diabatic transition ($\tau=25$ fs is the switch off for both pulses), reversing the sequence so that all of the population is transferred to $V_1(x)$. It is convenient that the oscillating wave packet is closer to $V_1(x)$ in order to achieve a highly selective fast diabatic transfer. This can also be controlled by timing the pulse duration in the plateau region. In this way we can achieve 39% squeezing in the example shown in Fig. 5. In fact, since the width is increasing for increasing periods in the LIP, it is possible to delay the diabatic transformation to achieve greater squeezing. However, although $V_1(x)$ and $V_3(x)$ are harmonic potentials, $U_0(x,t)$ is not harmonic, so there can be dispersion effects on the wave packet after several periods. The same procedure can also be implemented in the (I,b) sequence.

IV. SQUEEZING ON A REALISTIC MODEL: THE Rb_2 MOLECULE

In this section we apply one of the previous strategies to squeeze the vibrational wave packet in the ground state of the Rb_2 dimer. We choose the following electronic states: $X\,{}^1\Sigma_g^+[V_1(x)]$, $1\,{}^1\Pi_u[V_2(x)]$, and $2\,{}^1\Pi_g[V_3(x)]$, to prepare the LIP [33]. We concentrate here on the results obtained using the (C,b) sequence.

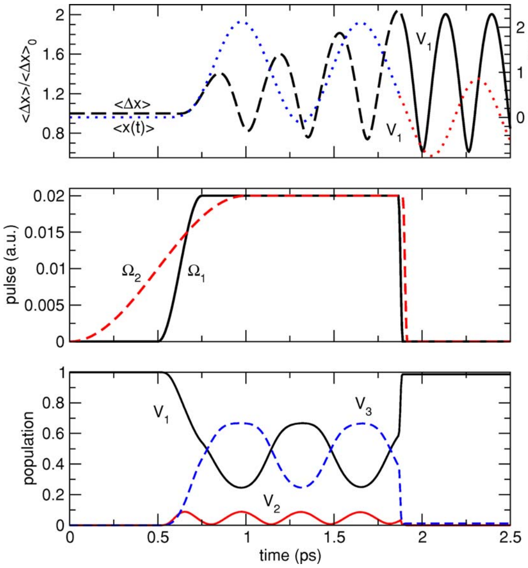

FIG. 5. (Color online) Dynamics of the ADS scheme (C,b) with crossing pulse profiles, for the HO model. The pulse crossings inhibit the full adiabaticity of the excitation, so that the wave packet oscillates and breathes in $U_0(x,t)$, before it is transferred to $V_3(x)$ where it is squeezed. In the upper frame we show the width of the wave packet (left scale) and the average position (right scale). Also shown are the pulse shapes and electronic populations.

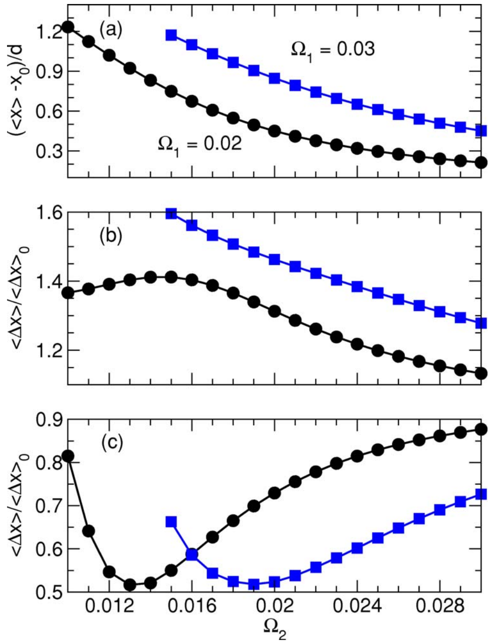

FIG. 6. (Color online) Maximal squeezing in Rb$_2$ as a function of the laser parameters. In (a) we show the equilibrium configuration of the $U_0(x)$ LIP that is prepared, in (b) the width of the LIP, which corresponds to the width of the wave packet for fully adiabatic transfer, and in (c) we show the final maximal squeezing achieved after the wave packet is transferred again to the ground potential. The results are shown for $\Omega_1=0.03$ (squares) and $\Omega_1=0.02$ (circles). All other parameters are fixed (see the text).

For realistic potentials one needs to find the best parameters that maximize the squeezing. However, this is not simple, since the mechanism is a two step process. Assuming perfect diabatic transfer, for harmonic potentials the dynamic squeezing depends entirely on the maximum stretching achieved on $U_0(x)$, so that it is only necessary to find the parameters that prepare a maximally wide LIP. This can be performed by static optimization [27] constraining the parameters within reasonable limits, so that $U_0(x)$ can be adiabatically accessed from the ground potential without needing too strong pulses. For anharmonic potentials, however, the dynamical effects of the anharmonicity over the width of the wave function are important and more difficult to assess, since they depend on the specific shape of the potential and on the initial wave packet, that is, on the region that the wave packet samples. In general, regions of high anharmonicity provoke fast dispersion of the packet, so that the squeezing, if any, is much reduced. This will occur if the equilibrium configuration of $U_0(x)$, $x_0^{(0)}$, is very displaced from the ground configuration, x_0, since then the diabatic (vertical) transition will place the wave packet near the dissociation limit of $V_1(x)$. It is therefore necessary to balance the need of a wide $U_0(x)$ and a small displacement $x_0^{(0)}-x_0$.

In Fig. 6 we show the relative width $\langle\Delta x\rangle/\langle\Delta x_0\rangle$ and displacement $(\langle x\rangle-x_0)/d$ (where d is the distance between the equilibrium configurations of the ground and second excited potentials) of the wave packet in $U_0(x)$ as a function of Ω_2. We have fixed the detuning $\Delta_1=\Delta_2=-0.005$ a.u., the pulse envelope ($\tau_1=1$ ps for both pulses), and the peak Rabi frequency of the first pulse $\Omega_1=0.03$ or 0.02 a.u. As Ω_2 becomes smaller, the width and the displacement of $U_0(x)$ increase, since for $\Omega_2\gg\Omega_1$, $U_0(x)$ correlates with $X\,{}^1\Sigma_g^+$, and for $\Omega_2\ll\Omega_1$, $U_0(x)$ correlates with $2\,{}^1\Pi_g$. Clearly, from this point of view one would like to prepare a LIP as similar as possible to the excited electronic state. The width of the wave packet can even be larger than that of $V_3(x)$ due to the additional dynamic stretching of the packet. However, the displacement increases at the same time.

In Fig. 6(c) we show the maximal dynamic squeezing achieved after the diabatic transformation. The minimum width (with 48% squeezing) is obtained at the first oscillation of the wave packet in $V_1(x)$ for $\Omega_2=0.019$ a.u. and $\Omega_1=0.03$ a.u., which does not come from the widest LIP. The dynamics of the ADS process is sketched for this particular case in Fig. 1, where we show the wave packets in the adiabatic (LIPs) and diabatic frames before and after the adiabatic and diabatic transformations, and at the time of maximal squeezing. A similar behavior is observed fixing $\Omega_1=0.02$ a.u., although with some losses in the final population transferred to $V_1(x)$. Since $V_1(x)$ is not harmonic, the time evolution of the wave packet is not simply periodic. The breathing motion leads to several (but not infinite) minima in the width of the wave packet at different oscillations. When $\Omega_2\ll\Omega_1$ the wave packet lands in highly anharmonic regions and the breathing is sustained during a few periods before dispersion occurs. For $\Omega_2\ll\Omega_1$ the motion is closer to the harmonic case, and in fact the maximun squeezing can occur after two or three oscillations of the wave packet. Obviously, after many more periods (~50–1000 depending on the wave packet and the potential) there will be revivals in both cases and the maximum squeezing will be again achieved [34–36].

Given this behavior, we hope that it should be possible to optimize the LIP based on simple static criteria. The function to minimize should balance the width and displacement of the potential [27], but the parameters of this balance should depend on the relative positions and widths of the laser-free electronic states of the molecule. In any case, the achieved squeezing is comparable or better than that found by the ISS scheme [28].

In this section we have shown the results of implementing the first strategy using the (C,b) sequence. Obviously we could have used the (I,r) sequence as well. On the other hand, the second strategy proposed in Sec. III B will not lead to major squeezing. Although for $\Omega_2 \ll \Omega_1$ the wave packet in $U_0(x)$ is wider than the width of $V_3(x)$ due to dynamical stretching, and the diabatic transition to $V_3(x)$ involves a small displacement, the difference in the widths is not large enough to induce appreciable squeezing with respect to the width of the initial wave function. The third strategy proposed in Sec. III C could be implemented as well, leading to similar final results as those shown here. Finally, since $V_3(x)$ is quite wide, one could think of going adiabatically to the electronic state, instead of stopping at the LIP, and reverting diabatically to $V_1(x)$. From the point of view of the adiabatic step there is no advantage. Fast strong adiabatic passage schemes like APLIP [20–22] or others, require the same pulse sequences but switching them off adiabatically; longer and weaker pulses could be used, as in stimulated Raman adiabatic passage [37–39], which exchange intensity per time duration as the main physical resources (and in fact reduce the pulse energy needs [39]). However, since the target state is an excited electronic state, there would be competition with fluorescence at longer times. There could be an advantage in the diabatic step if instead of doing the "vertical" two-pulse transition $V_3(x) \rightarrow V_1(x)$, one time-delays the pulses $V_3(x) \rightarrow V_2(x) \rightarrow V_1(x)$, so that the Franck-Condon region of the last step can be placed in regions of lower anharmonicity.

V. SUMMARY AND DISCUSSION

In this work we have compared adiabatic vs diabatic transformations applied to squeezing vibrational wave packets in diatomic or simple molecules, and we have proposed a scheme that combines the properties of both.

The adiabatic-diabatic squeezing mechanism is based on a two-step process, the first one involving an n pulse adiabatic transfer to an optimally wide (and not very displaced) light-induced potential; the second one involving an n pulse ultrafast diabatic transfer, so that the stretched wave packet squeezes dynamically by free evolution on a single chosen electronic potential. We have applied the scheme to two different systems, a set of symmetrically displaced harmonic oscillators and the Rb_2 dimer. We have shown that the ADS scheme performs typically better than previously proposed schemes, without recurring to optimal design methods [15,16]. In fact, the ADS scheme performs well even in relatively light molecules, like Na_2, or in systems where the widths of the potentials barely change, as in the SDHO, where the dynamic squeezing by the ISS simply cannot work, and the adiabatic squeezing gives poor results. The disadvantage of the method is that it requires strong nonresonant fields, as in adiabatic squeezing, and yet the squeezing is dynamic, so that it oscillates on the time scale of the vibrational motion, a few femtoseconds.

There have been several criticisms concerning the possibility of using strong nonresonant fields for adiabatic passage, due to the breakdown of the rotating-wave approximation, the effect of uncontrolled multiphoton transitions, and the role of rotation and ionization [40,41]. Although the intensity of the pulses used here (in the range of the $1-10\ \mathrm{TW/cm^2}$ depending on the transition dipole moments) is not exceedingly large, this limit cannot be reduced further in the ADS method. Perhaps the best solution is to use shorter pulses, whose time duration can be shifted into the femtosecond regime (as opposed to adiabatic squeezing [27]) even if at the expense of some population loss in the final electronic state.

We believe that the simplicity of the pulse sequences, and its general use, make the ADS scheme a valid tool for squeezing. Beyond the specific goal of this paper, the sequence of adiabatic and diabatic laser-driven transformations provide a broad arena where perhaps the dynamics of different type of systems can be controlled by means of physically simple mechanisms. To that end it is necessary to further explore the limits of adiabatic passage using ultrashort pulses (when the LIP is still a valuable representation of the dynamics), and the efficiency of pulse bandwidth vs pulse intensity resources. It is also necessary to extend the efficiency of adiabatic transformations in LIPs when the wave function is a nonstationary wave packet, and very importantly, to learn how to diabatically transfer wave packets between different LIPs.

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[32] In this process there is a rapid change of adiabatic potentials that can be facilitated because of the components of the LIPs that are involved. The initially prepared adiabatic wave packet moving in $U_0(x,t)$, $\Phi_0(x,t)$, approximately corresponds to $\cos[\theta(t)]\psi_1(x)-\sin[\theta(t)]\psi_3(x)$ [where $\theta(t)$ is the adiabatic angle of the mixing]. When both pulses have the same amplitude $\Phi_0(x,t)\approx\psi_1(x)-\psi_3(x)$. For large detuning, the almost unpopulated adiabatic wave packet in $U_+(x,t)$ is $\Phi_+(x,t)\approx\sin[\theta(t)]\psi_1(x)+\cos[\theta(t)]\psi_3(x)\approx\psi_1(x)+\psi_3(x)$. The fast and simultaneous switch off splits the wave packet in a linear superposition of $U_0(x,t)$ and $U_+(x,t)$, because the adiabatic wave packet is split into ψ_1 [moving in $V_1(x)$] and ψ_3 [moving in $V_3(x)$]. Finally, depending on the right phase of the pulses the final fast and simultaneous excitation can recombine the wave packets either to move back to $U_0(x,t)$ or to shift to $U_+(x,t)$, since the adiabatic wave packet depends on the relative phase of the wave functions. Although the relative populations are approximately equivalent, the shape of $U_0(x,t)$ and $U_+(x,t)$ differ; the first is wide and the second is narrow. Therefore there will be different breathing dynamics of the wave packet in each LIP. For small detuning the dynamics is not so simple (the switch on/off pulses must be longer) since $U_+(x,t)$ has an important contribution from $V_2(x)$, so that the splitting of the wave packet in both $V_1(x)$ and $V_3(x)$ involves partial excitation of $U_-(x,t)$.

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