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Ultrashort-pulse-train pump and dump excitation of a diatomic molecule

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An excitation scheme is proposed for transferring population between ground-vibrational levels of a molecule. The transfer is accomplished by pumping and dumping population with a pair of coherent ultrashort-pulse trains via a stationary state. By mismatching the teeth of the frequency combs associated with the pulse trains to the vibrational levels, high selectivity in the excitation, along with high transfer efficiency, is predicted. The pump-dump scheme does not suffer from spontaneous emission losses, it is insensitive to the pump-dump-train delay, and it requires only basic pulse shaping.

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I. INTRODUCTION

Molecular dynamics can be controlled and monitored by laser pulses, which can guide the molecule from an initial state toward a final target state [1]. Preparing a molecule in a predetermined internal energy state finds application in quantum computing [2], molecular spectroscopy [3], collision dynamics [4], photochemistry [5], among others. Several methods to control molecular dynamics have been proposed, but those that rely on short pulses offer a significant advantage by avoiding losses induced by spontaneous emission.

To control ground-state motion, a pair of time-delayed ultrashort pulses can be employed to perform a pump and dump transfer of population between vibrational levels of a molecule. With population initially in a vibrational eigenlevel of the molecule's ground electronic state, the pump pulse creates a nonstationary wave packet in an intermediate excited electronic state. A properly timed dump pulse then fully transfers the excited wave packet to a target-vibrational level in the ground electronic state. Optimal control techniques can be used to design the shape of the dump pulse that best drives the molecule to the target-vibrational level [6,7]. In the perturbative weak-excitation regime, analytical solutions for the globally optimal control pulse can be found [8,9]. But in the strong excitation limit, when a large amount of population is transferred between vibrational levels, the optimal pulse shape is frequently found only by numerical optimization [10]. Often, the optimal pulse shape is difficult to interpret and too complex to implement experimentally [11].

Two methods for controlling quantum systems that are conceptually simpler were recently theoretically proposed [12,13]. Both methods combine optimal control in the weak-excitation regime and the principle of coherent accumulation [14,15] to perform Raman transitions between molecular-vibrational levels through nonstationary wave-packet excitation. Efficient and robust population transfer was demonstrated in both cases. One of these methods uses a coherent train of weak pump-dump pairs of shaped ultrashort pulses [12]. The weak-pulse pairs allow an analytical description of the control problem, while the coherent accumulation of excitation between pulse pairs provides an efficient excitation of the target-vibrational level. The weak excitation promoted by an individual pulse pair and the spectral selectivity afforded by the pulse train overcome difficulties found in several other excitation methods, such as leakage of population to nearby vibrational levels [12]. Pumping and dumping occurs in a very short time scale, so the method is immune to spontaneous emission losses. Knowledge of the excited molecular potential is required in order to correctly design the dump pulses. Pump and dump pulses need to be properly timed, and the relative phase between successive pulse pairs needs to be stabilized. The other method [13] explores a combination of piecewise adiabatic transfer concepts and coherent train excitation. Population transfer was demonstrated through a slow variation of the intensity envelope of the pump and dump-pulse trains, as well as through a slow variation of the excitation phase. The method is interferometrically sensitive to the pump and dump delay, and requires phase stabilization of both pulse trains. Even without properly shaping the pulses, the scheme can achieve high transfer efficiencies (80%) if spontaneous emission is not included in the model. Because the overall excitation occurs in a time scale comparable to the spontaneous lifetime of the excited state, including spontaneous emission losses in the model lowers the transfer efficiency of the scheme.

In this paper, I propose another approach for controlling the molecular-vibrational level in the ground electronic potential of a diatomic molecule. The present approach shares with the other two methods described earlier [12,13] the use of the spectral selectivity of ultrashort-pulse trains and the concept of coherent accumulation of excitation. It differs from them in that the population transfer between ground-vibrational levels of the molecule is done via an excited *stationary* state. As will be discussed, here the scheme proposed has several desirable features: It does not require previous knowledge of the molecular potentials, it is insensitive to the pump-dump-train delay, and it is not disturbed by spontaneous emission. Population transfer efficiencies approaching 100%, with high selectivity, are predicted.

Section II of this paper offers a conceptual description of the proposed pump and dump excitation scheme. Section III introduces the model used to describe the interaction between the molecule and the ultrashort-pulse trains. In Sec. III, the molecular equations of motion are numerically solved, and the results are presented and discussed. Section IV concludes the paper.

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II. PROPOSED PUMP AND DUMP SCHEME

Figure 1 illustrates the excitation of a homonuclear diatomic molecule by two femtosecond pulse trains. The molecule consists of a lower (ground) and an upper (excited) manifold of vibrational energy levels belonging to distinct electronic states. The first pulse train (pump) excites dipole transitions between the ground and excited-vibrational states, transferring population from the first to the latter. For high pulse-repetition rates, the molecule does not decay during excitation by the pump train.

The dynamics of excitation of the molecule by a pulse train with terahertz repetition rate was described in Ref. [16]. Due to its ultrabroad spectrum, each femtosecond pulse from the train can simultaneously excite several vibrational levels of the molecule. A vibrational wave packet is created in the excited electronic state. The multiple wave packets created by the many pulses in the train interfere. By properly mismatching the pulse-repetition period to the vibrational period of the excited molecule, the wave-packet interference can be made destructive such that a single-vibrational eigenlevel is selectively excited by the train. Viewed in the frequency domain, this selective excitation is possible because the spectrum of the train consists of a comblike structure of narrow frequency peaks. Mismatching the pulse-repetition period and the molecule's vibrational period corresponds to mismatching the comb's teeth to the vibrational levels. Only one comb tooth is kept resonant to a single excited-vibrational eigenlevel.

Each pulse in the train creates a small excitation in the molecule. For terahertz pulse-repetition rates, the molecule does not decay in between pulses, and the excitation accumulates coherently from one pulse to the next. As reported in Ref. [16], because of the selectivity afforded by the pulse train, the multilevel molecule behaves effectively as a two-level system. The population in the target $\bar{\upsilon}$ vibrational level is closely described by $P_{\bar{\upsilon}} \approx \sin^2(\theta/2)$, where

$$\theta \equiv \alpha_{\bar{\upsilon}0} \int_{-\infty}^{\infty} f(s)\, ds \tag{1}$$

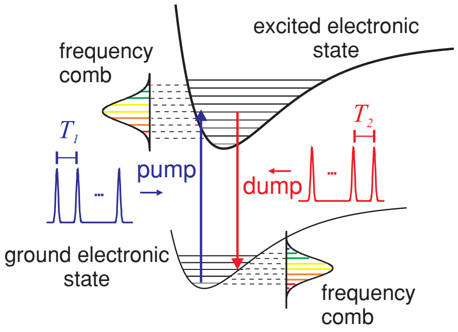

FIG. 1. (Color online) A diatomic molecule interacting with a pair of ultrashort-pulse trains. The pump train, with repetition period T_1, fully transfers the population initially in the ground- vibrational level to a single-vibrational level in the excited state. The dump train (repetition period T_2) returns the population to the ground electronic state, but at a different vibrational level. To excite the molecule with high selectivity, the teeth of the frequency combs associated with the pulse trains should be mismatched to the vibrational levels in both electronic states. Only one tooth of the comb is kept resonant to a single-vibrational level in both pump and dump cases.

is the pulse train area, $f(s)$ is the train temporal envelope, and $\alpha_{\bar{\upsilon}0}$ is a Rabi frequency. Full excitation of the molecule, with high selectivity, is achieved when the train area θ is approximately π.

These results should be equally valid for deexcitation of an initially excited molecule. Therefore, the second pulse train (dump) shown in Fig. 1 should send the excited population back down to the ground electronic state, again with high efficiency and selectivity. By tuning the dump pulses differently from the pump pulses, the final ground-vibrational state will be different from the initial-vibrational state. The dump-pulse train also has a high pulse-repetition rate, and by working with pump-dump-train delays several orders of magnitude shorter than the spontaneous decay lifetime of the excited state, the molecule will not suffer any significant decay during neither intratrain nor intertrain excitations.

III. INTERACTION MODEL

For simplicity, the relevant molecular potentials are modeled as Morse potentials, and the dependence of the electronic dipole moments with internuclear distance is ignored. The effects of molecular rotation are also neglected, and I will limit the investigation to the excitation of pure states in the molecule. Although this molecular model may not be quantitatively accurate enough for precise predictions, it retains the main features required to demonstrate the proposed scheme.

In the interaction-picture state basis, the molecular state at an arbitrary time t is given by $|\psi(t)\rangle = \sum_n a_n(t)\exp(-i\omega_{gn}t)|g,n\rangle + \sum_j b_j(t)\exp(-i\omega_{ej}t)|e,j\rangle$. The equations of motion governing the time evolution of the ground $[a_j(t)]$ and excited $[b_n(t)]$ probability amplitudes are, in the rotating-wave approximation: 2

$$\dot{a}_n = (i/2)e^{i\omega_{gn}t}\sum_{j=0}^{\upsilon_b}[\alpha_{jn}f^*(t) + \Omega_{nj}g^*(t)]b_j(t)e^{-i\omega_{ej}t}, \tag{2a}$$

$$\dot{b}_j = (i/2)e^{i\omega_{ej}t}\sum_{n=0}^{\upsilon_a}[\alpha_{jn}f(t) + \Omega_{nj}g(t)]a_n(t)e^{-i\omega_{gn}t} - (\gamma/2)b_j(t). \tag{2b}$$

Here, $\alpha_{jn} \equiv 2\langle n,g|\hat{d}|e,j\rangle E_p^0/\hbar$ and $\Omega_{nj} \equiv 2\langle j,e|\hat{d}|g,n\rangle E_d^0/\hbar$ are real Rabi frequencies of the pump and dump electric fields, respectively; $\upsilon_{a,b}$ are the number of eigenstates contained in each of the two electronic manifolds; ω_{ej} and ω_{gn} are the eigenfrequencies of the excited- and ground-vibrational levels, respectively, with $\omega_{g0} \equiv 0$. Population in the excited-vibrational states decay spontaneously out of the system at a rate given by γ.

The shape of the pump-pulse train is described by

$$f(t) = \sum_m \exp\left[\frac{-(t-mT_1)^2}{\tau^2} - \frac{m^2}{N^2}\right]e^{-i\omega_p t}. \tag{3}$$

The individual pulses in the train have identical Gaussian temporal envelopes and are uniformly spaced in time with a repetition period given by T_1. Their widths are determined by τ. The train also has an overall Gaussian profile, and N is a measure of the number of pulses it contains. The pulses in the train are indexed by m, which takes on both positive and negative values. The pulses have carrier frequency

ω_p tuned to a preselected vibrational level in the excited electronic state of the molecule. A similar temporal shape is also assumed for the dump-pulse-train envelope $g(t)$, with carrier frequency $\omega_d \neq \omega_p$ and repetition period T_2. Pulse-train envelopes described by Eq. (2), with femtosecond pulse widths and terahertz repetition rates, can be created with existing pulse-shaping techniques [17].

IV. NUMERICAL RESULTS AND DISCUSSION

Two excitation scenarios for the proposed pump-dump scheme were simulated and will be presented. In the first scenario, the molecule starts in its lowest vibrational level, and population is transferred to a higher-lying vibrational level in the ground electronic state. And in the second scenario, the pump-dump scheme is applied to create deeply bound molecules from loosely bound Feshbach molecules. The equations of motion [Eqs. (2)] are solved numerically in both cases.

For the first scenario, a potassium molecule was considered. The ground and excited electronic states were the $X\ ^1\Sigma_g^+$ and $A\ ^1\Sigma_u^+$ states, respectively. The A state has a vibrational period close to 500 fs and a population decay rate $\gamma^{-1} = 28$ ns. The eigenfrequencies and Franck-Condon factors for the X and A states were calculated from the potentials of Ref. [18]. The pump-carrier frequency was set to $\omega_p = 35\,389$ cm^{-1}, resonant with the $|g,0\rangle \rightarrow |e,10\rangle$ transition. The $|e,10\rangle$ vibrational level is at the peak of the Franck-Condon factors for transitions from the ground-vibrational level, but transitions with lower Franck-Condon factors can also be excited by adjusting the pulse amplitude or the number of pulses in the train [16]. The dump-carrier frequency was set to $\omega_d = 31\,544$ cm^{-1}, resonant with the $|e,10\rangle \rightarrow |g,15\rangle$ transition.

For both pump and dump trains, I used $\tau = 50$ fs, $N = 7$, and $T_1 = T_2 = 560$ fs, resulting in the electric field displayed in Fig. 2. The two trains are delayed with respect to each other by 22.4 ps. The amplitudes of the trains were adjusted so their area, as given by Eq. (1), was approximately π. Since the $|e,10\rangle \rightarrow |g,15\rangle$ transition has a smaller Franck-Condon factor than the $|g,0\rangle \rightarrow |e,10\rangle$ transition, the peak amplitude of the dump train is higher than that of the pump train. Because of the high pulse-repetition rates, both pump and dump trains correspond to very coarse frequency combs, containing roughly only seven comb teeth within their spectra's full width at half maximum.

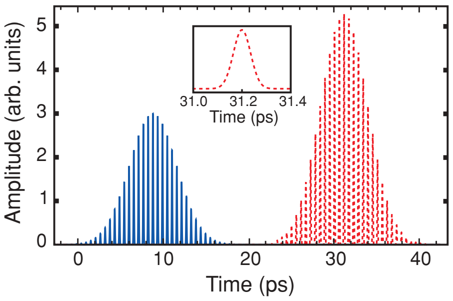

FIG. 2. (Color online) Pump (solid blue) and dump (dashed red) ultrashort-pulse trains. The inset shows one of the pulses from the dump train. Both trains consist of Gaussian pulses with an amplitude full width at half maximum of approximately 71 fs.

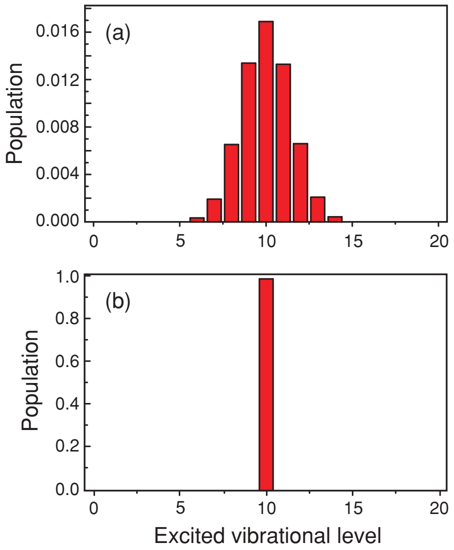

FIG. 3. (Color online) Vibrational population distribution in the electronic A state excited by (a) a single 71-fs-wide Gaussian pulse and (b) a train of such pulses.

Figure 3(a) shows the population excited by a single pulse from the pump train. With a pulse-amplitude full width at half maximum of approximately 71 fs, a single pulse has a spectral bandwidth broad enough to simultaneously and coherently excite more than seven vibrational levels of the molecule. However, a train of such pulses, with its repetition period properly mismatched from the molecule's vibrational period, excites a single-vibrational level, as shown in Fig. 3(b).

The population dynamics in the ground and excited electronic states is presented in Fig. 4(a). The pump train transfers all the ground-state population to the excited A state in a piecewise manner, with each pump pulse removing a small amount of population from the initial ground state. Population accumulates coherently from one pulse in the train to the next, until it is fully transferred to the excited state. Likewise, the dump pulse sends the population back down to the ground state, again small steps at a time. The final molecular state consists of single ground-vibrational level as shown in Fig. 4(b). Because the train-molecule interaction is completed in less than 40 ps, the molecule does not suffer any significant decay during this time. Over 99% of the population is transferred to the target ground-vibrational level. From $P \approx \sin^2(\theta/2)$, it is seen that the excitation is robust with respect to train-area errors. A 20% error in the area, due to fluctuations in the dump-pulse amplitude, for example, will decrease the transfer efficiency to 90%; this estimate was confirmed by a numerical simulation. The target ground level can be chosen by properly selecting the dump-carrier frequency. Figure 4(b) also shows the excitation of the $|g,11\rangle$-vibrational level by setting $\omega_d = 32\,506$ cm^{-1}, thus demonstrating the high degree of selectivity afforded by the scheme.

To quantify the fidelity of the excitation, I used a generalization of the achievement factor $\mathcal{A}$, defined by $\mathcal{A}^2 = \mathrm{Tr}(\hat{\rho}\hat{\rho}_T)/(\mathrm{Tr}\hat{\rho}^2\mathrm{Tr}\hat{\rho}_T^2)^{1/2}$, where $\hat{\rho}$ is the density operator associated with the final actual state and $\hat{\rho}_T$ is that of the

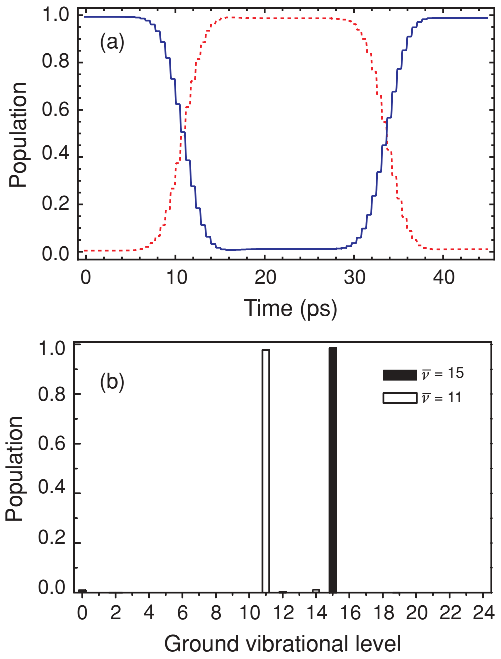

FIG. 4. (Color online) (a) Population dynamics in the ground (solid blue) and excited (dashed red) electronic states of the potassium molecule under excitation by the pulse trains shown in Fig. 2. (b) Final population distribution among the vibrational levels of the ground X state for two target levels: $\bar{\nu} = 15$ and $\bar{\nu} = 11$.

target state [19]. Since I am only considering pure states, and the target state is a fully excited single-vibrational level, the achievement factor simplifies to

$$\mathcal{A} = \frac{|a_{\bar{\nu}}|}{\left(\sum_{n=0}^{\nu_a} |a_n|^2\right)^{1/2}}, \tag{4}$$

where $a_{\bar{\nu}}$ is the actual probability amplitude of the target ground-vibrational level ($n = \bar{\nu}$) excited by the train, and $\sum_n |a_n|^2$ is the actual total population in the ground electronic state. An achievement factor of $\mathcal{A} = 1$ indicates that only the target-vibrational level in the ground electronic state was excited. $\mathcal{A} = 0$ means no excitation of the target level, although other ground-vibrational levels may have been excited.

The selective excitation relies on destructive interferences between excited wave packets, and as such, it is interferometrically sensitive to the pulse-repetition period. Figure 5(a) plots the total population in the ground electronic state as well as the excitation fidelity as a function of the dump-repetition period T_2. Large dips (labeled e) in the population curve are seen when the repetition period is approximately an integer or half-integer multiple of the excited-vibrational period (≈497 fs). In such cases, the dump train is inefficient at populating the ground state, although it does it with high fidelity. Dips (labeled g) in the fidelity curve are also seen for dump periods that are integer or half-integer multiples of the ground-vibrational period (≈429 fs), meaning that more than one ground-vibrational level is excited. Excitation efficiency is high (>80%) in most of these cases. The vertical dotted line indicates the value of T_2 used in the simulations of Fig. 4. Several other values of the dump-repetition period can be found for which both high efficiency and fidelity can be achieved simultaneously. In general, correctly setting the repetition period is critical, although a few regions of less sensitivity to the precise value of T_2 can be seen in Fig. 5(a).

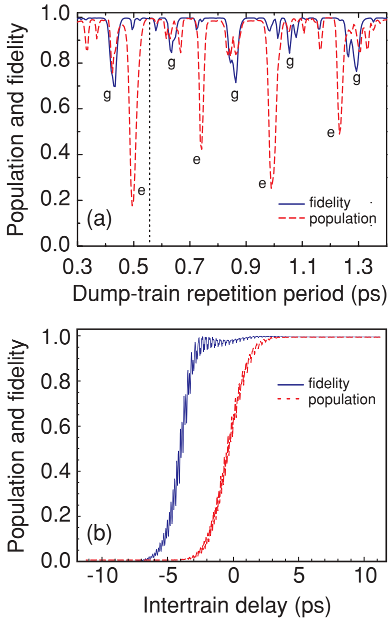

FIG. 5. (Color online) Population in the ground electronic state and fidelity of the excitation as a function of (a) the dump-train repetition period and (b) the delay between pump and dump trains.

The pump-dump scheme is quite immune to the intertrain delay. The pump train excites a stationary state in the excited electronic state, and therefore, the time the dump train begins interacting with the excited molecule is irrelevant in most cases. Figure 5(b) illustrates how the fidelity and ground-state population vary with the intertrain delay, defined as the time delay between the center pulses in both trains. The pulse trains are described by the parameters of Fig. 2. Both trains have an amplitude half width at half maximum of approximately 3.5 ps. When the intertrain delay becomes shorter than this half width, the final ground-state population starts being affected by the delay. However, the fidelity remains high even at negative delays. The reason is that, after just a few pulses, the comb spectral structure of the pump is relatively well defined; a stationary state is already excited by the first few leading pump pulses in the pump train [16].

In the second excitation scenario that was investigated, the piecewise pump-dump scheme was applied to a rubidium molecule. The goal was to create a deeply bound molecule in the ground $X\ {}^1\Sigma_g^+$ electronic state starting from a weakly bound molecule in the same electronic potential. (Weakly bound molecules can be created from ultracold atoms by magnetically or optically tuning a Feshbach resonance [20].) Population was transferred between ground-vibrational levels through the intermediate excited $A\ {}^1\Sigma_u^+$ electronic state. The potentials of Ref. [21] were used to calculate the relevant eigenfrequencies and Franck-Condon factors for the ground and electronic states. The pump-carrier frequency was set to $\omega_p = 36\,596\ \mathrm{cm}^{-1}$, resonant with the $|g,130\rangle \rightarrow |e,157\rangle$ transition. And the dump-carrier frequency was chosen to be $\omega_p = 42\,418\ \mathrm{cm}^{-1}$, resonant with the $|e,157\rangle \rightarrow |g,45\rangle$

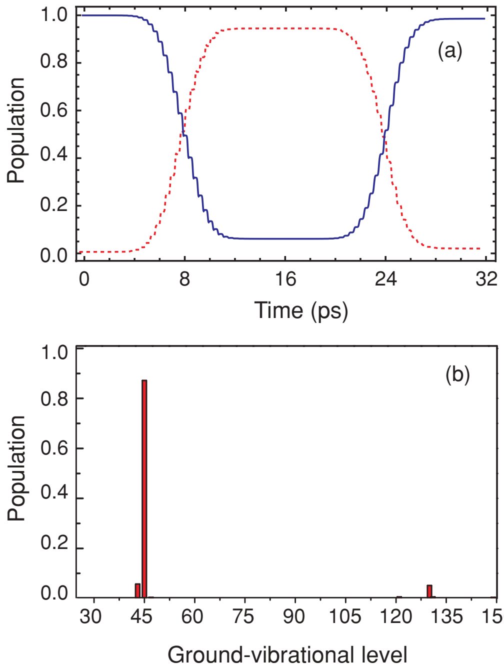

FIG. 6. (Color online) (a) Population dynamics in the ground (solid blue) and excited (dashed red) electronic states of the rubidium molecule under excitation by pump and dump trains of ultrashort pulses. (b) Final population distribution among the vibrational states of the ground X state. Population was initially in the $|g,130\rangle$ level, and the target level was the $|g,45\rangle$ level.

transition. For both pulse trains, I chose $N = 7$, $\tau = 80$ fs, and $T_1 = T_2 = 410$ fs. The pump- and dump-train areas were set to approximately π, and the intertrain delay to 8.2 ps. The population excitation dynamics and the final ground-state population distribution are shown in Fig. 6. The final population in the target-vibrational level was 87%, and the fidelity was $A = 0.94$. Little over 1% of the population remained in the excited electronic state at the end of excitation. Even though there is a high density of vibrational levels around the initial $|g,130\rangle$ state, the pump-dump trains were capable of transferring population with high efficiency and fidelity to the target-vibrational level.

In both excitation scenarios, similar pulse trains were used for pumping and dumping. But, in general, the trains may need to have different repetition periods due to the different vibrational spacing of nearby levels around the initial and target ground states, as well excited states. The present two-state model neglects the possibility of excitation from the first excited electronic state to a higher-lying state. Such a loss channel could be avoided by setting the phase of the driving fields orthogonal to the transition dipole, as suggested in Ref. [7]. Additionally, the repetition periods of both trains could be further adjusted so that all comb teeth are out of resonance with any vibrational level of the higher electronic state. This last possibility will be investigated in future work.

V. CONCLUSIONS

I proposed a pump-dump scheme based on femtosecond pulse trains to transfer population between ground-vibrational levels of a molecule via an excited stationary state. The scheme relies on mismatching the pulse-repetition period of both trains to the molecule's ground- and excited-vibrational periods. Close to 100% population transfer between vibrational levels with high fidelity is predicted.

The proposed scheme requires only basic pulse shaping to generate the pulse train and does not rely on knowledge of the molecular potentials. Even though a simple Morse potential was used to model the molecular electronic states, the method should be likewise applicable to coupled potentials, since the excitation pulses do not need to be shaped according to the spectral shape and phase of the transition dipole moments. As such, the present scheme is quite general and should be applicable to a large variety of molecular systems.

The scheme is largely insensitive to the intertrain delay, and therefore, there is no need to precisely synchronize the pump and dump trains. The population transfer can be completed in a very short time scale (tens of picoseconds or shorter), so it does not suffer from spontaneous decay losses, nor should it be disturbed by collisions between molecules. Properly adjusting the pulse-repetition period for both trains is critical, but by scanning the repetition periods, one can maximize the efficiency and fidelity of the transfer.

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