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Laser cooling of internal molecular degrees of freedom for vibrationally hot molecules

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We present an approach to laser cooling of internal molecular degrees of freedom for vibrationally hot molecules using a sequence of ultrashort laser pulses. It is assumed that the molecules initially occupy different vibrational states with a substantial portion of the molecules being in excited vibrational states. We show that the ultimate aim of increasing the vibrational ground-state population through a reduction of the system's entropy can be achieved through a multistep process. In the first step, we design an ultrashort laser pulse that selectively transfers most of the population of the excited vibrational states to an excited electronic surface; then the field is switched off and the system allowed to relax until most of the excited electronic state population has decayed due to spontaneous emission. By repeating this procedure a few times, the entropy of the system can be substantially reduced and the population of the vibrational ground state increased considerably, even if the lifetimes of the excited electronic states are much greater than the length of a control pulse, i.e., if dissipative effects are negligiable on the time scales of coherent control.

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I. INTRODUCTION

Laser cooling of atoms to 10^{-9} K [1,2] and Bose-Einstein condensation [3] of ultracold atomic vapors has been one of the most exciting developments in physics in recent years. Cooling molecules, however, has proved to be much more challenging due to the complicated internal vibrational and rotational structure. The only experiments so far that have produced molecules at sub-mK temperatures used photoassociation of ultracold atoms. Many different variations of this technique exist [4–8] but one common feature of all these techniques seems to be the fact that the molecules produced, while translationally cold, are in vibrationally excited states. Nikolov *et al.* recently reported in [7] results from a two-step photoassociation scheme that produces ground-state molecules with greatly improved efficiency, but even in their approach a considerable fraction of the molecules are in excited vibrational states. Cooling the internal molecular degrees of freedom is important since molecules in excited vibrational states are likely to undergo inelastic collisions with other atoms or molecules in the trap resulting in the ejection of the molecule and its collision partner. On the other hand, the rate constants for such collisions are relatively small when the vibrational quantum number is small [9]. Furthermore, cooling the internal molecular degrees of freedom, i.e., reducing the populations of the excited rotational and vibrational states is also a prerequisite for creating a molecular condensate.

In this paper we focus our attention on cooling of the vibrational degrees of freedom of molecules. Given a distribution of vibrational states, the main obstacle to cooling is the second law of thermodynamics: cooling in this case requires a reduction of the entropy of the system, which can only happen if the system is coupled to another system that serves as entropy sink. Several techniques to reduce the entropy of the system have been proposed [10–12].

In the evaporative cooling approach, a fraction of the system is sacrificed to carry away entropy. For instance, in order to cool the vibrational degrees of freedom on the electronic ground surface of a molecule, the population of the vibrationally excited states on the electronic ground surface can be transferred to an excited electronic surface using an optimally designed laser pulse and subsequently removed. This technique is quite effective but has obvious shortcomings. Superior methods such as heat pump cooling of internal molecular degrees of freedom by coupling the system to a bath mode have been proposed, however, these methods did not utilize radiation as the ultimate entropy sink.

Recent work by Tannor *et al.* [12] has shown that the major obstacle to utilizing spontaneous emission to carry away the entropy of the system is the lifetime of the excited electronic states. The decay of the excited electronic states due to spontaneous emission is generally too slow to be relevant on the time scales of coherent control. If one could speed up the dissipative processes artificially then coherent control might work. The problem is that although it is possible to influence spontaneous emission by applying strong electromagnetic fields [13], it is in general difficult to control spontaneous emission and thus speed up dissipation. In the following we shall therefore explore a modification of the standard one-step optimal control approach, which takes advantage of the dark states discovered by Tannor *et al.*, to avoid this problem.

II. QUANTUM STATISTICAL MECHANICS MODEL

Our basic quantum statistical mechanics model is similar to [12], i.e., we consider the vibrational energy levels of a diatomic molecule on the electronic ground surface as well as on an excited electronic surface and denote by $\hat{\rho}_g$ the vibrational density operator on the electronic ground surface and by $\hat{\rho}_e$ the vibrational density operator on the excited electronic surface. $\hat{\rho}_i$ represents the correlations between both surfaces. The density operator of the combined system thus has the form

$$\hat{\rho}=\hat{\rho}_g\otimes\hat{P}_g+\hat{\rho}_e\otimes\hat{P}_e+\hat{\rho}_i\otimes\hat{S}_+ +\hat{\rho}_i^{\dagger}\otimes\hat{S}_- \tag{1}$$

$$\doteq \begin{pmatrix} \hat{\rho}_e & \hat{\rho}_i \\ \hat{\rho}_i^\dagger & \rho_g \end{pmatrix}, \tag{2}$$

where $\hat{P}_g$ and $\hat{P}_e$ represent the projection operators onto the electronic ground and excited surfaces, respectively, and $\hat{S}_\pm$ represent the raising and lowering operators from one surface to the other.

The total Hamiltonian of the system consists of the internal Hamiltonian $\hat{H}_0$ and an interaction term $\hat{V}(t)$,

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t). \tag{3}$$

The zeroth-order internal Hamiltonian is the sum of the surface Hamiltonians $\hat{H}_g$ and $\hat{H}_e$, i.e.,

$$\hat{H}_0 = \hat{H}_g \otimes \hat{P}_g + \hat{H}_e \otimes \hat{P}_e \tag{4}$$

$$\doteq \begin{pmatrix} \hat{H}_e & 0 \\ 0 & \hat{H}_g \end{pmatrix}, \tag{5}$$

and in the dipole approximation the interaction term is

$$\hat{V}(t) = \hat{\mu} \otimes [\hat{S}_+ f(t) + \hat{S}_- f^*(t)] \tag{6}$$

$$\doteq \begin{pmatrix} 0 & f(t)\hat{\mu} \\ f^*(t)\hat{\mu} & 0 \end{pmatrix}, \tag{7}$$

where $\hat{\mu}$ is the transition dipole operator and $f(t)$ the time-dependent control field. If the aim is to control a diatomic molecule then we might choose a control field that is linearly polarized along the molecular axis. In this case f can be assumed to be real valued and we have simply

$$\hat{H} = \hat{H}_0 + f(t)\hat{H}_1 \tag{8}$$

with

$$\hat{H}_1 \doteq \begin{pmatrix} 0 & \hat{\mu} \\ \hat{\mu} & 0 \end{pmatrix}. \tag{9}$$

The evolution of the system is governed by the quantum Liouville equation [14]

$$i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)] - i\hbar \Gamma(\hat{\rho}(t)), \tag{10}$$

where Γ is the dissipation (super-)operator.

III. LIOUVILLE SPACE REPRESENTATION

The space of linear operators on the Hilbert space of pure states $\mathcal{H}$ forms itself a Hilbert space, in the literature often called Liouville space. For practical purposes, we shall assign each Hilbert space operator $\hat{A}$ (represented by a $N \times N$ matrix, where N is the dimension of $\mathcal{H}$) a Liouville ket $|A\rangle\rangle$ represented by a N^2 column vector obtained by rearranging the matrix elements of $\hat{A}$. Let $|\rho(t)\rangle\rangle$ denote the Liouville space representation of $\hat{\rho}(t)$ and define the Liouville operators $\mathcal{L}_0$, $\mathcal{L}_1$ by the bijective correspondences

$$\mathcal{L}_0 |\rho\rangle\rangle \leftrightarrow [\hat{H}_0, \hat{\rho}], \tag{11}$$

$$\mathcal{L}_1 |\rho\rangle\rangle \leftrightarrow [\hat{H}_1, \hat{\rho}]. \tag{12}$$

Then the total Liouvillian is

$$\mathcal{L} = \mathcal{L}_0 + f(t)\mathcal{L}_1 - i\hbar \mathcal{L}_D, \tag{13}$$

where $\mathcal{L}_D$ is the Liouville space dissipation operator, and the equation of motion in Liouville space is simply

$$i\hbar \frac{\partial}{\partial t} |\rho(t)\rangle\rangle = \mathcal{L} |\rho\rangle\rangle. \tag{14}$$

IV. OPTIMAL CONTROL FORMULATION

Application of optimal control theory requires the choice of a functional whose value at a certain target time is to be maximized. This functional has to reflect both the goal of the control process and the constraints imposed by the equations of motion, etc. Among the many possible choices, we consider the following functional [15–19]:

$$W(f, \rho_v, A_v) = W_1(\rho_v) - W_2(f, \rho_v, A_v) - W_3(f), \tag{15}$$

where

$$W_1(f) = \langle A(t_F) \rangle = \langle \langle A | \rho_v(t_F) \rangle \rangle, \tag{16}$$

$$W_2(f, \rho_v, A_v) = \int_{t_0}^{t_F} \left\langle \left\langle A_v(t) \left| \frac{\partial}{\partial t} + \frac{i}{\hbar} \mathcal{L}(t) \right| \rho_v(t) \right\rangle \right\rangle dt, \tag{17}$$

$$W_3(f) = \frac{\lambda}{2} \int_{t_0}^{t_F} |f(t)|^2 dt. \tag{18}$$

W_1 is the expectation value of the target operator $\hat{A}$, which we wish to maximize at the target time t_F. W_2 ensures that the quantum Liouville equation is satisfied. W_3 is a penalty term that constrains the fluence, i.e., the total energy of the pulse. $\rho_v(t)$ and $A_v(t)$ are variational trial functions that must satisfy the boundary conditions

$$\rho_v(t_0) = \rho(t_0) = \rho_0, \quad A_v(t_F) = A. \tag{19}$$

V. SOLUTION OF THE CONTROL PROBLEM

Our ultimate goal is to maximize the population of the vibrational ground state on the electronic ground surface. However, if the system is initially in thermal equilibrium or any mixed state, for which the vibrational ground-state population on the electronic ground surface is larger than the population of any of the vibrationally excited states, then the vibrational ground-state population can only increase through dissipative effects since the kinematical constraint of unitary evolution [20] effectively prohibits any further increase of the ground-state population for Hamiltonian dynamics. The problem with taking advantage of dissipation to achieve the control objective is that for real molecules the dissipative terms arising from spontaneous emission are usually too small to be relevant on the time scales of coherent control. Hence, a different approach is necessary.

Instead of maximizing the vibrational ground-state population, our aim is to transfer as much of the populations of the excited vibrational states on the electronic ground surface to the excited electronic surface without affecting the vibrational ground-state population on the electronic ground surface. To accomplish this, we choose our observable to be

$$\hat{A}=\hat{P}_e+(|1\rangle\langle 1|\otimes\hat{P}_g) \tag{20}$$

$$\doteq\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{21}$$

and solve the optimal control problem outlined above. In order to find an optimal pulse that maximizes the expectation value of $\hat{A}$ at a specified target time subject to the dynamical and fluence constraints, we employ a modified (noniterative) version of an entangled feedback algorithm [15,16]. Then we turn the laser off and allow the system to relax for a period of time that depends on the lifetimes of the excited electronic states. During this period the population of all vibrational states on the electronic ground surface will increase due to decay of the excited electronic states by spontaneous emission.

While this leads to the desired increase of the population of the ground state, unfortunately, there will also be some degree of repopulation of the vibrationally excited states on the electronic ground surface. However, the populations of these states tend to be less than their initial populations. Hence, repeating this procedure several times leads to a monotonic increase of the population of the target state without evaporation of the system.

VI. ILLUSTRATIVE COMPUTATIONS

We apply this approach to a model of Na_2. To keep our preliminary computations reasonable, we restrict ourselves to two electronic states, the electronic ground-state configuration $X\,{}^1\Sigma_g^+$ and the first excited state $A\,{}^1\Sigma_u^+$, and consider only the lowest three vibrational energy levels for each electronic state. The vibrational energy levels are computed for $n=1,2,3$ using the Morse oscillator formula

$$E_n=\omega_e\left(n-\frac{1}{2}\right)-\omega_e x_e\left(n-\frac{1}{2}\right)^2+T_e. \tag{22}$$

For the electronic ground surface, we have $\omega_e=159.124\,\mathrm{cm}^{-1}$ and $\omega_e x_e=0.7254\,\mathrm{cm}^{-1}$ and $T_e=0\ \mathrm{cm}^{-1}$. For the excited electronic state, the spectroscopic constants are $\omega_e=117.323\,\mathrm{cm}^{-1}$, $\omega_e x_e=0.3576\,\mathrm{cm}^{-1}$, and $T_e=14680.58\,\mathrm{cm}^{-1}$ [21]. Thus, the internal surface Hamiltonians are

$$\hat{H}_g=\hbar\omega_0\begin{pmatrix} 0.4989 & 0 & 0\\ 0 & 1.4897 & 0\\ 0 & 0 & 2.4715 \end{pmatrix}, \tag{23}$$

$$\hat{H}_e=\hbar\omega_0\begin{pmatrix} 92.6258 & 0 & 0\\ 0 & 93.3596 & 0\\ 0 & 0 & 94.0880 \end{pmatrix}, \tag{24}$$

where $\omega_0=2\pi c(100\,\mathrm{cm/m})\times 159.124\,\mathrm{cm}^{-1}=2.9973\times 10^{13}\,\mathrm{s}^{-1}$.

To obtain approximate values for the transition probabilities from the nth vibrational level on the electronic ground surface to the mth vibrational level on the excited electronic surface we compute the Frank-Condon factors

$$g_{mn}=\left[\int \psi_m^{e*}\psi_n^g dR\right]^2, \tag{25}$$

where ψ_m^e is the vibrational wave function corresponding to the mth vibrational level on the excited electronic surface and ψ_n^g is the vibrational wave function corresponding to the nth vibrational level on the electronic ground surface. This gives rise to

$$\hat{\mu}^2=0.1|p_{XA}|^2\begin{pmatrix} 0.01905 & 0.1193 & 0.3737\\ 0.1193 & 0.5278 & 1.0840\\ 0.03737 & 1.084 & 1.246 \end{pmatrix}, \tag{26}$$

where p_{XA} equals the electronic transition moment for the transition $X\to A$.

To estimate the probability that the nth vibrational state on the excited electronic surface decays into the mth vibrational state on the electronic ground surface by spontaneous emission, we set

$$\gamma_{mn}=\frac{1}{\tau}\frac{g_{mn}}{g_{m1}+g_{m2}+g_{m3}}, \tag{27}$$

where τ is the lifetime of the excited electronic state, which is approximately $\tau=12.5\,\mathrm{ns}$ for disodium [21]. This gives rise to the population relaxation operator

$$\hat{\gamma}\doteq\omega_0\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0\\ 0.00009922 & 0.0006214 & 0.001946 & 0 & 0 & 0\\ 0.0001838 & 0.0008128 & 0.001670 & 0 & 0 & 0\\ 0.0003685 & 0.001069 & 0.001229 & 0 & 0 & 0 \end{pmatrix} \tag{28}$$

from which the Liouville space dissipation operator can easily be derived.

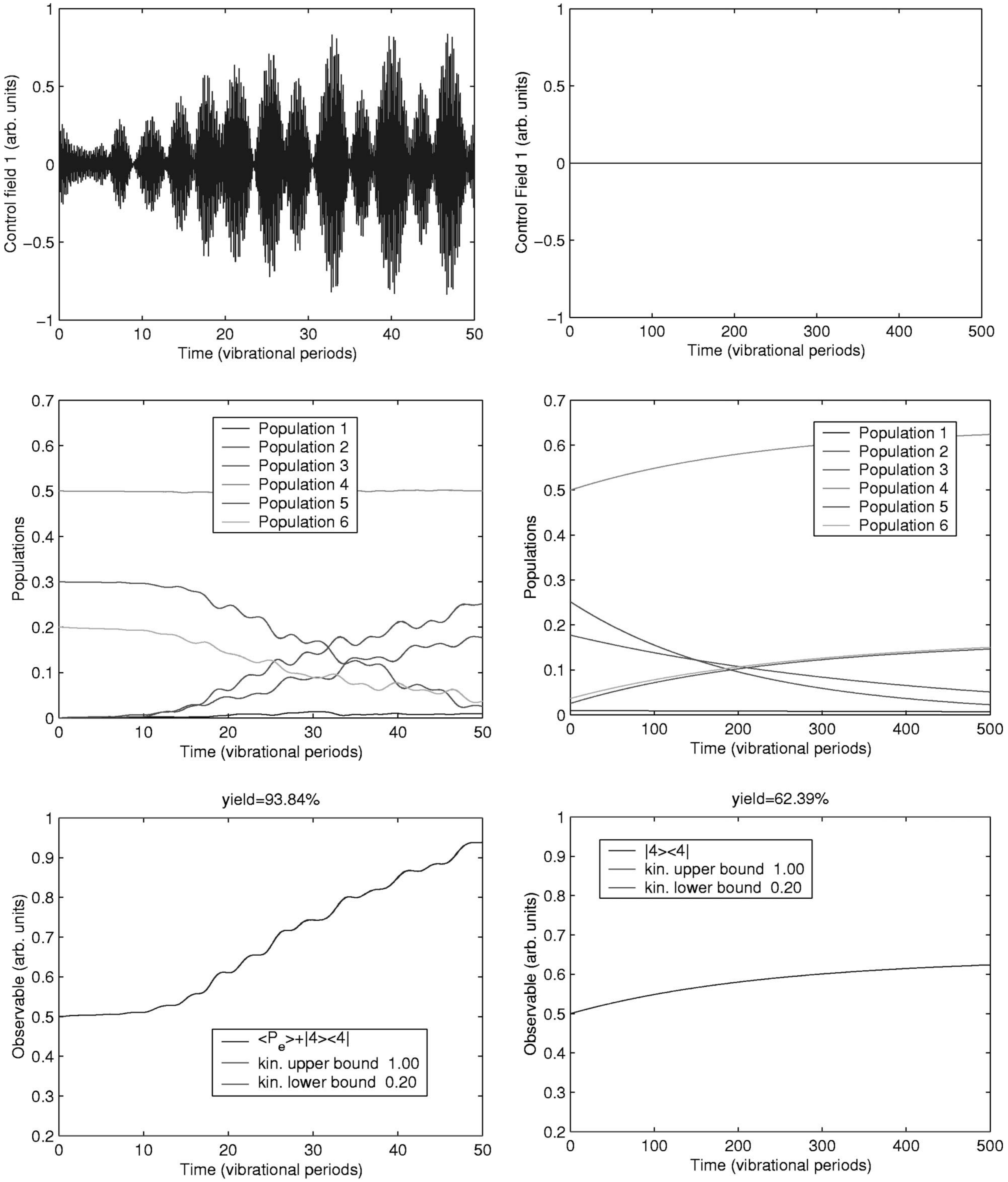

FIG. 1. Initial excitation and relaxation step.

The following figures show the results of a preliminary computation for disodium. For illustration purposes only, we assume that the initial ensemble is

$$\hat{\rho}_{g,0}=\begin{pmatrix} 0.5 & 0 & 0 \\ 0 & 0.3 & 0 \\ 0 & 0 & 0.2 \end{pmatrix}, \quad \hat{\rho}_{e,0}=\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{29}$$

i.e., initially 50% of the molecules are in the vibrational ground state, 30% in the first excited vibrational state, and 20% in the second excited vibrational state on the electronic ground surface. The population of the excited electronic surface is zero. Due to space constraints, only the results of the first and last steps of our multistep control procedure are shown in Figs. 1 and 2.

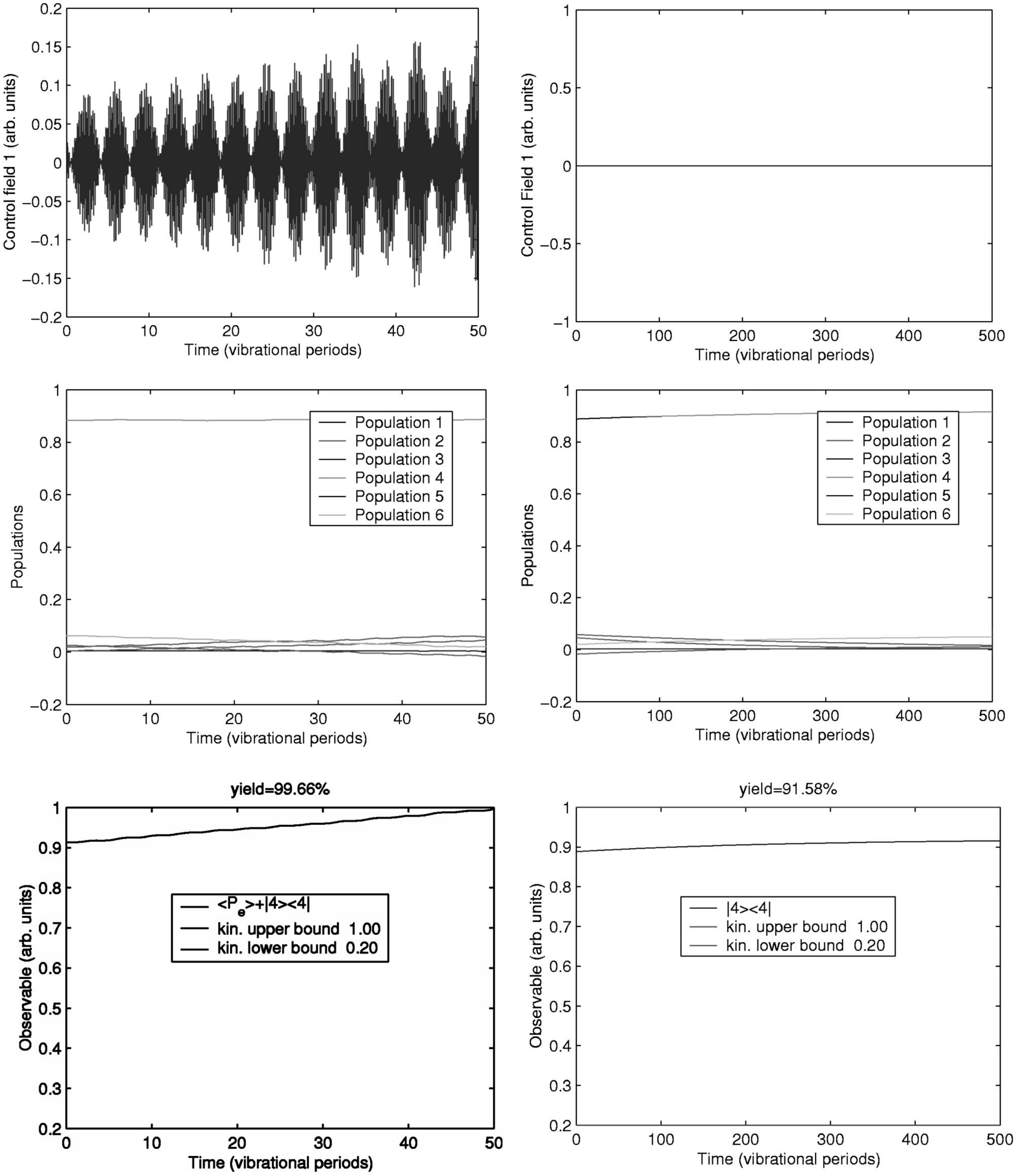

FIG. 2. Final excitation and relaxation step.

Notice that after only seven excitation-relaxation steps the population of the vibrational ground state on the electronic ground surface is about 90% without evaporation, using only spontaneous emission as entropy sink. If we were to remove the population of the excited electronic surface after step 7A then over 99% of the remaining molecules would be in the vibrational ground state (on the electronic ground surface) with less than 10% of the initial ensemble sacrificed due to evaporation.

VII. CONCLUSION

We have presented an approach to laser cooling of the vibrational degrees of freedom for molecules that combines optimal control by coherent laser pulses and uncontrolled spontaneous emission to reduce the entropy of the system. One of the main advantages of this approach is that it does not require the lifetimes of the excited electronic states to be on the order of a few vibrational periods as our computations for disodium show. Furthermore, since entropy is carried away by spontaneous emission, it is not necessary to sacrifice a part of the system to achieve cooling.

The proposed technique relies on one's ability to find control pulses that *selectively* transfer the populations of excited states without affecting the vibrational ground-state population on the electronic ground state. The effectiveness of this approach depends on the transition probabilities between vibrational states on different electronic surfaces. As long as the transition probabilities are sufficiently different, this method should be able to increase the vibrational ground-state population starting with an arbitrary distribution of vibrational states.

In principle, our approach is not limited to cooling vibrational degrees of freedom. However, the aforementioned need for sufficiently different transition probabilities might make it difficult to select the rovibrational ground state, i.e., it is conceivable that this technique would produce a large population of molecules in the vibrational ground state but with a distribution of rotational states, which would then need to be cooled separately.

Although our illustrative computations were done using only three vibrational levels on two electronic surfaces corresponding to the electronic ground state and the first excited state for disodium, it is in principle possible to repeat the computations using actual values for the vibrational distributions obtained by photoassociation experiments. All that is required is accurate information about the energy levels of the highly excited states as well as good estimates for the transition probabilities between different states and the lifetimes of the excited states.

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