Laser cooling of internal molecular degrees of freedom

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Abstract

We present a new approach to laser cooling of internal molecular degrees of freedom using a sequence of ultrashort laser pulses. Instead of attempting to maximize the vibrational ground-state population in a single step using an optimal control field, we use an optimally shaped, ultra-short laser pulse to transfer most of the population of the excited vibrational states to an excited electronic surface; then we switch the field off and allow the system to relax until most of the excited electronic state population has decayed due to spontaneous emission. We repeat this procedure a few times until the vibrational ground state population has reached a desired minimum value of ca. 90%. The advantages of this procedure are that it relies mainly on spontaneous emission to reduce the entropy of the system, there is virtually no population loss on the ground surface at the final time, and unlike one-step optimization procedures using coherent control, it is effective even if the lifetime of the excited electronic states is much longer than the length of the pulse.

1 Introduction

Laser cooling of translational degrees of freedom of atoms to 10^{-9} K and Bose-Einstein condensation [1] of ultra-cold atomic vapors has been one of the most exciting recent developments in physics. As far as cooling molecular vapors is concerned, however, progress has been much more limited and BEC of molecular vapors has not yet been experimentally achieved. Among the obstacles is the far greater complexity of the problem. Cooling the translational degrees of freedom is considerably more difficult for molecules than it is for atoms. To complicate the matter further, molecules have in addition vibrational and rotational degrees of freedom that have to be considered as well. For instance, several recent experiments that succeeded in producing translationally cold molecules by photo-association of ultracold atoms [2, 3] produced molecules that were vibrationally hot. This shows that cooling the translational degrees of freedom is not sufficient in the molecular case and that the rotational and vibrational degrees of freedom need to be cooled as well.

The main obstacle to cooling is the second law of thermodynamics. Cooling 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 [4, 5, 6]. In the evaporative cooling approach, a fraction of the system is sacrificed to carry away excess 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. Other 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 do not utilize radiation as the ultimate entropy sink.

Recent work by Tannor et. al. [6] has shown that the major obstacle to utilizing spontaneous emission to carry away the excess 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 timescales of coherent control. However, it is possible to take advantage of this fact to achieve vibrational cooling by modifying the standard one-step optimal control approach.

2 Quantum Statistical Mechanics Model

Our basic model is similar to [6]. 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

$$\begin{aligned}\hat{\rho} &= \hat{\rho}_g \otimes \hat{P}_g + \hat{\rho}_e \otimes \hat{P}_e + \hat{\rho}_i \otimes \hat{S}_+ + \hat{\rho}_i^\dagger \otimes \hat{S}_- \qquad (1)\\ &\doteq \begin{pmatrix} \hat{\rho}_e & \hat{\rho}_i \\ \hat{\rho}_i^\dagger & \rho_g \end{pmatrix}, \qquad (2)\end{aligned}$$

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 0th order internal Hamiltonian is the sum of the surface Hamiltonians $\hat{H}_g$ and $\hat{H}_e$, i.e.,

$$\begin{aligned} \hat{H}_0 &= \hat{H}_g \otimes \hat{P}_g + \hat{H}_e \otimes \hat{P}_e && (4) \\ &\doteq \begin{pmatrix} \hat{H}_e & 0 \\ 0 & \hat{H}_g \end{pmatrix}. && (5) \end{aligned}$$

In the dipole approximation the interaction term is

$$\begin{aligned} \hat{V}(t) &= \hat{\mu} \otimes (\hat{S}_+ f(t) + \hat{S}_- f^*(t)) && (6) \\ &\doteq \begin{pmatrix} 0 & f(t)\hat{\mu} \\ f^*(t)\hat{\mu} & 0 \end{pmatrix} && (7) \end{aligned}$$

where $\hat{\mu}$ is the transition dipole operator and $f(t)$ the time-dependent control field. If f is real-valued then

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

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

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

where Γ is the dissipation (super-)operator.

3 Liouville Space Representation

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

$$\begin{aligned} \mathcal{L}_0|\rho\rangle\rangle &\leftrightarrow [\hat{H}_0, \hat{\rho}], && (11) \\ \mathcal{L}_1|\rho\rangle\rangle &\leftrightarrow [\hat{H}_1, \hat{\rho}], && (12) \end{aligned}$$

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

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

4 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 [7]:

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

where

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

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

and

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

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 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

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

5 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 [8] 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* disturbing the vibrational ground state population on

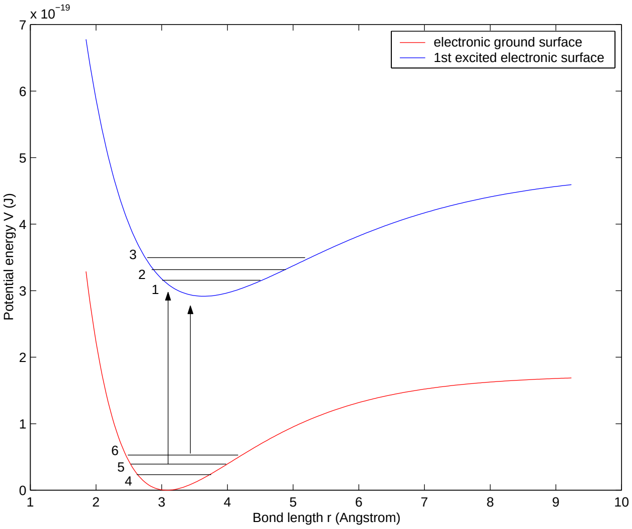

Figure 1: Schematic of controlled excitation step

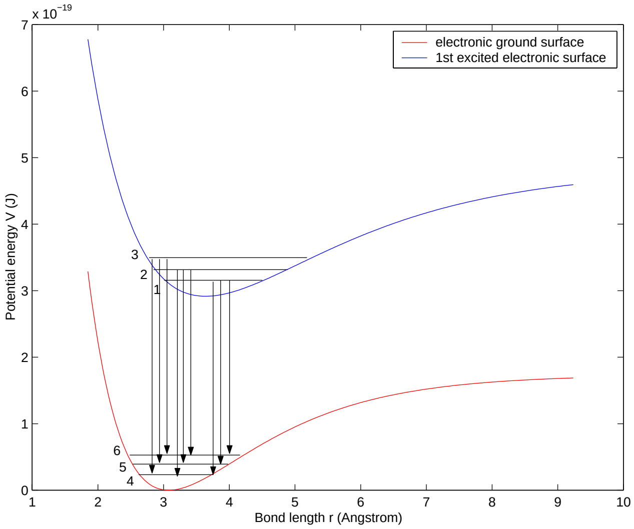

Figure 2: Schematic of free relaxation step

the electronic ground surface (see Fig. 1). To accomplish this, we choose the observable

$$\hat{A} = \hat{P}_e + \left(|1\rangle\langle 1| \otimes \hat{P}_g\right) \doteq \mathrm{diag}(1,1,1,1,0,0) \qquad (20)$$

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 (non-iterative) version of an entangled feedback algorithm [9, 10]. 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. (see Fig. 2).

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

6 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

$$E_n = \omega_e\left(n - \frac{1}{2}\right) - \omega_e x_e\left(n - \frac{1}{2}\right)^2 + T_e. \qquad (21)$$

For the electronic ground surface, we have $\omega_e = 159.124$ cm^{-1} and $\omega_e x_e = 0.7254$ cm^{-1} and $T_e = 0$ cm^{-1}. For the excited electronic state, the spectroscopic constants are $\omega_e = 117.323$ cm^{-1}, $\omega_e x_e = 0.3576$ cm^{-1} and $T_e = 14680.58$ cm^{-1} [11]. Thus, the internal surface Hamiltonians are

$$\hat{H}_g = \hbar\omega_0 \begin{pmatrix} 0.4989 & 0 & 0 \\ 0 & 1.4897 & 0 \\ 0 & 0 & 2.4715 \end{pmatrix}, \qquad (22)$$

$$\hat{H}_e = \hbar\omega_0 \begin{pmatrix} 92.6258 & 0 & 0 \\ 0 & 93.3596 & 0 \\ 0 & 0 & 94.0880 \end{pmatrix} \qquad (23)$$

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

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

$$g_{mn} = \left[\int {\psi_m^e}^* \psi_n^g dR\right]^2 \qquad (24)$$

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

$$\hat{\mu} = 0.1|p_{XA}|^2 \begin{bmatrix} 0.01905 & 0.1193 & 0.3737 \\ 0.1193 & 0.5278 & 1.0840 \\ 0.3737 & 1.084 & 1.246 \end{bmatrix} \qquad (25)$$

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

$$\gamma_{mn} = \frac{1}{\tau} \frac{g_{mn}}{g_{m1} + g_{m2} + g_{m3}}. \tag{26}$$

where τ is the lifetime of the excited electronic state, which is approximately $\tau = 12.5$ ns for disodium [11]. This gives rise to the population relaxation operator $\hat{\gamma} \doteq \omega_0(\gamma_{mn})$ where $\gamma_{11} = 0.00009922$, $\gamma_{12} = 0.0006214$, $\gamma_{13} = 0.001946$, $\gamma_{21} = 0.0001838$, $\gamma_{22} = 0.0008128$, $\gamma_{23} = 0.00167$, $\gamma_{31} = 0.0003685$, $\gamma_{32} = 0.001069$, $\gamma_{33} = 0.001229$, from which the Liouville space dissipation operator can easily be derived.

Figs 3 and 4 show the results of a computation for disodium for the initial ensemble

$$\hat{\rho}_{g,0} = \begin{pmatrix} 0.5 & 0 & 0 \\ 0 & 0.3 & 0 \\ 0 & 0 & 0.2 \end{pmatrix}, \quad \hat{\rho}_{e,0} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{27}$$

i.e., initially 50% of the molecules are in the vibrational ground state, 30% in the first excited vibrational state and 20% in the 2nd excited vibrational state on the electronic ground surface. The population of the excited electronic surface is initially zero.

Due to space constraints, only the first and the last step of our multi-step control procedure are shown in Figs 3 and 4. In both figures the top left graph shows the control field for the controlled excitation step. The graph below shows the evolution of the populations of the vibrational energy levels on the ground and the excited electronic surface. Observe the almost monotonic decrease of the populations of the excited vibrational states on the electronic ground surface while the vibrational ground state population remains practically constant and the populations of the vibrational states on the excited electronic surface increase almost monotonically. The expectation value of the observable during the controlled excitation is plotted at the bottom left. The graphs in the right half of the figure correspond to the uncontrolled relaxation period. The control field (top right) is zero during this period. The populations of the excited electronic state decrease due to spontaneous emission of photons while the populations of the vibrational energy levels on the electronic ground surface increase accordingly (middle, right). The time evolution of the vibrational ground state population on the electronic ground surface, i.e., the target observable, is shown in the last graph (bottom-right). Notice the monotonic increase during the uncontrolled relaxation period. Observe that after only seven excitation-relaxation steps the population of the vibrational ground state on the electronic ground surface is almost 90% *without evaporation* using only spontaneous emission as entropy sink. If the population of the excited electronic surface was removed after the last excitation step 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 by evaporation.

7 Conclusion

We have presented a new approach to laser cooling of the vibrational degrees of freedom for molecules that combines both optimal control by coherent laser pulses and 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. Since entropy is carried away by spontaneous emission, substantial cooling can be achieved without sacrificing part of the system. The results can be improved further by adding a final evaporation step to remove the small percentage of molecules that remain in vibrationally excited states even after several controlled excitation-relaxation steps.

References

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STEP 1A: EXCITATION

STEP 1B: RELAXATION

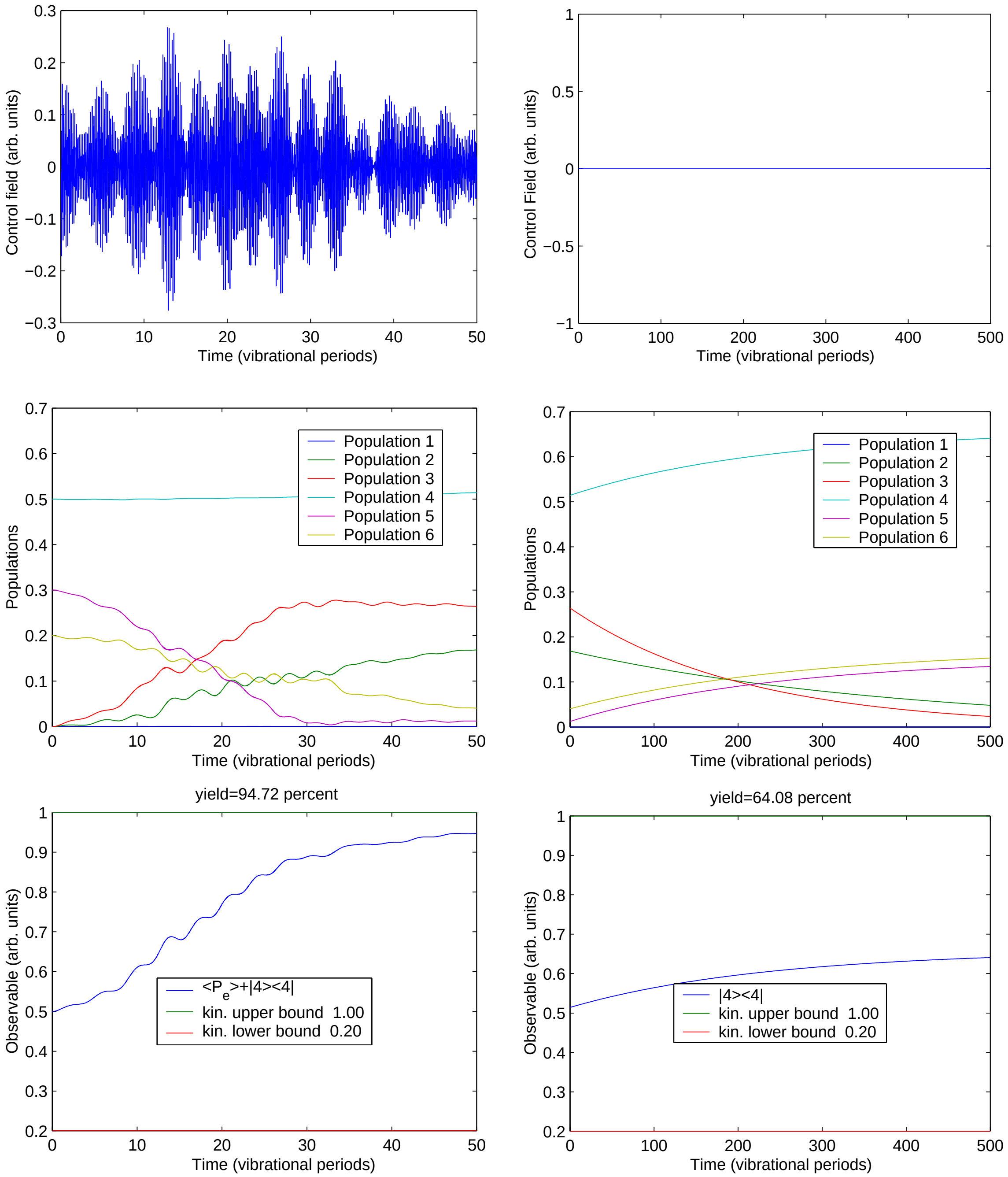
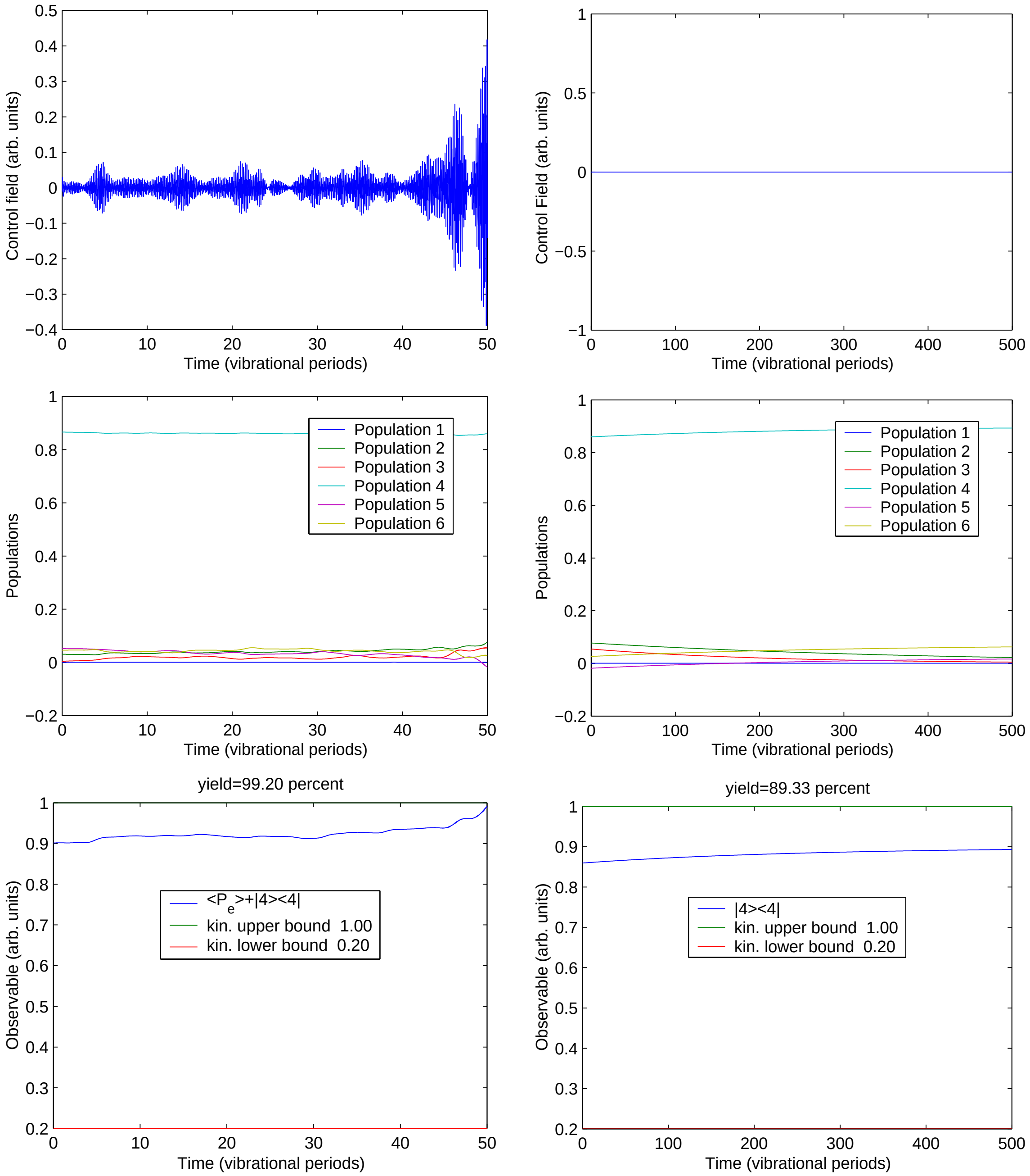


Figure 3: Results of the first controlled excitation and free relaxation step for disodium.



Step 7A: Excitation

Step 7B: Relaxation

Figure 4: Results of the final controlled excitation and relaxation step for disodium