Laser cooling of internal degrees of freedom. II.

Allon Bartana and Ronnie Kosloff
Department of Chemistry and the Fritz Haber Institute for Molecular Dynamics, Hebrew University of Jerusalem, Israel

David J. Tannor
Department of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

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Theoretical progress in the cooling of internal degrees of freedom of molecules using shaped laser pulses is reported. The emphasis is on general concepts and universal constraints. Several alternative definitions of cooling are considered, including reduction of the von Neumann entropy, $-tr\{\hat{\rho}\log\hat{\rho}\}$ and increase of the Renyi entropy, $tr\{\hat{\rho}^2\}$. A distinction between intensive and extensive considerations is used to analyse the cooling process in open systems. It is shown that the Renyi entropy increase is consistent with an increase in the system phase space density and an increase in the absolute population in the ground state. The limitations on cooling processes imposed by Hamiltonian generated unitary transformations are analyzed. For a single mode system with a ground and excited electronic surfaces driven by an external field it is shown that it is impossible to increase the ground state population beyond its initial value. A numerical example based on optimal control theory demonstrates this result. For this model only intensive cooling is possible which can be classified as evaporative cooling. To overcome this constraint, a single bath degree of freedom is added to the model. This allows a heat pump mechanism in which entropy is pumped by the radiation from the primary degree of freedom to the bath mode, resulting in extensive cooling. © *1997 American Institute of Physics.* [S0021-9606(97)02304-0]

I. INTRODUCTION

Laser cooling of a microscopic object, such as a single ion in a trap or an ensemble of molecules is at the forefront of atomic physics.[1–3] The ultra-cold temperatures obtained enhance the quantum nature of matter, the most dramatic effect being Bose condensation.[4] In contrast to atomic cooling, laser cooling of molecules has not been demonstrated yet. This study is devoted to the understanding of molecular cooling. A few mechanisms have been proposed.[5] Some of them, by analogy with atomic cooling, rely on spontaneous emission as the key cooling element.[6] The present study is devoted to cooling mechanisms based on the coherent properties of light. This study contains a critical evaluation of our previous study,[7] whose result has been a new cooling mechanism.

Theoretical analysis of laser cooling requires the understanding of the interplay between thermodynamic and quantum considerations. Thermodynamic analysis of macroscopic cooling processes reveals that the main obstacle to cooling is imposed by the second law. The entropy reduced by the cooling process must be dumped in an appropriate reservoir or entropy sink. The mechanism of entropy disposal is then used to classify the cooling scenario. Evaporative cooling constitutes one such class. This process occurs in an open thermodynamic system where a fraction of the system is sacrificed to carry away the excess entropy. Heat pump cooling constitutes the second class. In a heat pump an external source of work is used to drive entropy from the system to an entropy sink. It will be shown that this classification is useful for microscopic cooling scenarios.

Constructing a microscopic model for the cooling process is based on a series of partitions of the system. The first of these partitions separates the matter and the radiation degrees of freedom. Specifically in this study, the radiation is employed to control the evolution of the matter. With this model in mind, the radiation does not serve as an entropy sink. This is in contrast to atomic cooling where through spontaneous emission the light serves as the primary entropy sink. This assumption allows a simplified theoretical description based on the state of the matter $\hat{\rho}$, and the evolution is generated by the Liouville-von Neumann equation:

$$\frac{\partial\hat{\rho}}{\partial t}=-\frac{i}{\hbar}[\hat{\mathbf{H}},\hat{\rho}]+\mathscr{L}_D(\hat{\rho}), \tag{1.1}$$

$\hat{\mathbf{H}}$ is the Hamiltonian which includes the radiation as a time dependent field:

$$\hat{\mathbf{H}}=\hat{\mathbf{H}}_{\mathbf{s}}-\hat{\mu}\cdot\mathscr{E}(t). \tag{1.2}$$

Here $\hat{\mathbf{H}}_{\mathbf{s}}$ is the system Hamiltonian, $\mathscr{E}(t)$ is a time dependent field and $\hat{\mu}$ is the transition dipole operator. For an open quantum system which is in contact with an external bath $\mathscr{L}_D$ in Eq. (1.1) is the generator of dissipative dynamics.[8–10]

Energy balance relations are one of the bridging factors between thermodynamics and quantum mechanics. With the partition described by Eq. (1.1) the rate of change of energy in the system becomes:

$$\frac{dE}{dt}=\left\langle\frac{\partial\hat{\mathbf{H}}}{\partial t}\right\rangle+\langle\mathscr{L}_D(\hat{\mathbf{H}})\rangle. \tag{1.3}$$

This equation can be interpreted as the time derivative of the first law of thermodynamics,[11–14] where the power absorbed or emitted from the radiation field becomes

$$\mathscr{P}=\left\langle \frac{\partial \hat{\mathbf{H}}}{\partial t} \right\rangle = -\langle \hat{\mu} \rangle \cdot \frac{\partial \mathscr{E}}{\partial t} \tag{1.4}$$

and $\dot{Q}=\langle \mathscr{L}_D(\hat{\mathbf{H}}) \rangle$ becomes the heat transfer current.

The second partition distinguishes between the molecular nuclear and the electronic degrees of freedom. Specifically two electronic surfaces are employed enabling the system to be driven through optical transitions. The state of such a system using pseudo-spin notation is described as

$$\hat{\rho}=\hat{\rho}_g \otimes \hat{\mathbf{P}}_g + \hat{\rho}_e \otimes \hat{\mathbf{P}}_e + \hat{\rho}_c \otimes \hat{\mathbf{S}}_+ + \hat{\rho}_c^\dagger \otimes \hat{\mathbf{S}}_- = \begin{pmatrix} \hat{\rho}_e & \hat{\rho}_c \\ \hat{\rho}_c^\dagger & \hat{\rho}_g \end{pmatrix}, \tag{1.5}$$

where $\hat{\rho}_g$, $\hat{\rho}_e$ are the nuclear populations on the ground and excited surfaces, respectively, and $\hat{\rho}_c$ is the nuclear coherence between these surfaces. $\hat{\mathbf{P}}_{\mathbf{e/g}}$ is the projection on the upper and lower electronic surface and $\hat{\mathbf{S}}_\pm$ are the raising and lowering operators of the electronic transition.

For the two surface model, the Hamiltonian becomes

$$\begin{aligned} \hat{\mathbf{H}} &= \hat{\mathbf{H}}_\mathbf{g} \otimes \mathbf{P}_\mathbf{g} + \hat{\mathbf{H}}_\mathbf{e} \otimes \hat{\mathbf{P}}_\mathbf{e} - \epsilon(t)\hat{\mu} \otimes \hat{\mathbf{S}}_+ - \epsilon(t)^* \hat{\mu} \otimes \hat{\mathbf{S}}_- \\ &= \begin{pmatrix} \hat{\mathbf{H}}_\mathbf{e} & -\epsilon(t)\hat{\mu} \\ -\epsilon(t)^* \hat{\mu} & \hat{\mathbf{H}}_\mathbf{g} \end{pmatrix}, \end{aligned} \tag{1.6}$$

where $\hat{\mathbf{H}}_{\mathbf{e/g}}$ are the surface Hamiltonians, $\epsilon(t)$ is a time dependent control function, and $\hat{\mu}$ is the electronic transition dipole.

Complete controllability requires a complex control function $\epsilon(t)$. To realize this possibility with radiation two independent polarization components of the transition dipole operator are required together with simultaneous control of the time dependent amplitude and polarization of the radiation field. These conditions can then be translated to the phase and amplitude of the control function ϵ.

With the partition described by Eq. (1.6), the power absorbed or emitted from the field becomes[7]

$$\mathscr{P}=-2\,\mathrm{Real}\left(\langle \hat{\mu} \otimes \hat{\mathbf{S}}_+ \rangle \frac{\partial \epsilon}{\partial t} \right). \tag{1.7}$$

Analysis of this equation reveals that control of the power direction is obtained by adjusting the phase of the field to the phase of the instantaneous transition dipole expectation. For example by choosing the phase angle of the time derivative of the field to be $\pi/2$ out of phase with the instantaneous transition dipole phase angle, zero power conditions are obtained. This instantaneous control strategy can be employed to control the change of other quantities such as the ground surface energy $\langle \hat{\mathbf{H}}_\mathbf{g} \rangle$. These possibilities have been explored in our previous paper.[7]

The final partition defines the boundary between the system and the bath, or more precisely the entropy sink. One possibility which has been explored in our previous paper[7] is to use the upper electronic manifold as the entropy sink. It will be shown that this choice leads to evaporative cooling. Another possibility is to distinguish between primary (system) and secondary (bath) nuclear degrees of freedom. This scenario, as will be shown in section III allows for a heat pump cooling mechanism.

This study also explores the consequences of a finite heat sink. In this regime the dynamics can be simplified by omitting the dissipative term $\mathscr{L}_D$ from the equation of motion. Under these conditions the evolution operator becomes unitary, a fact that will be exploited in the analysis.

The consequence of an infinite heat bath in a simple 3-level cooling model has been studied.[15] It was shown that an isothermal partition between the system and bath can be constructed based on the weak coupling limit. This construction enables one to consider the radiation as an entropy sink through spontaneous emission. Such a possibility is beyond the scope of the present study, since coherent control which is the main agent of the cooling process is only realizable for very fast processes. Under these conditions the rate of spontaneous emission is too slow to be important.

The present study is an integral part of the field of coherent control of molecular processes.[16–22] The objective of cooling can be defined as a target function for optimal control theory. Optimization toward this target is to be obtained within a finite time interval. This construction is close in spirit to finite time thermodynamics where a thermodynamic objective is to be obtained in finite time.[23–25] The introduction of time means that the *rate* of cooling can be defined. This suggests an interpretation of the third law of thermodynamics stating that the rate of cooling vanishes when the absolute zero is approached.

II. THEORY

A. Definitions of cooling

Cooling a macroscopic object is easily identified as lowering its temperature. For a microscopic object the definition of cooling is more involved. One reason is the result of large fluctuations which cause temperature to be ill defined. In addition, a microscopic object is more likely to be in a thermal disequilibrium state.

To set a rigorous framework for defining the cooling process, an ensemble of *noninteracting* microscopic objects is considered. This ensemble can be open, meaning that the particle number is subject to change. This situation leads to a distinction between intensive and extensive variables. Considering specifically the partition between the upper and lower electronic surfaces, Eq. (1.5), the ground state energy extensive variable becomes: $E_g=tr\{\hat{\mathbf{H}}_\mathbf{g} \otimes \hat{\mathbf{P}}_\mathbf{g} \hat{\rho}\}$, and the fraction number of particles in the ground surface will be: $N_g/N=tr\{\hat{\mathbf{P}}_\mathbf{g}\hat{\rho}\}$. The intensive energy variable becomes the average energy per particle: $E_g=\langle \hat{\mathbf{H}}_\mathbf{g} \rangle / \langle \hat{\mathbf{P}}_\mathbf{g} \rangle$. Under this partition, an intensive (normalized) ground surface density operator can be defined: $\overline{\rho_g}=\hat{\rho}_g / \langle \hat{\mathbf{P}}_\mathbf{g} \rangle$.

For a microscopic system the entropy replaces temperature as a primary observable since it can be defined for a system in disequilibrium. The point of view adopted is of information theory where the entropy is a measure of dispersion in the probability distribution of an ensemble.[26,27] In

quantum mechanics this information depends on the choice of the measurement. The definition employed is therefore that entropy is a measure of dispersion in the outcome of a complete quantum observation. Such an observation is related to the observable chosen. Of particular importance for cooling is the energy observable. The information entropy related to a complete energy observation becomes

$$\sigma_E = -\sum_n p_n \log p_n , \tag{2.1}$$

where p_n is the expectation of the n'th energy eigenvalue $p_n = tr\{\hat{\mathbf{P}}_\mathbf{n}\hat{\rho}\}$ where $\hat{\mathbf{P}}_\mathbf{n} = |n\rangle\langle n|$ and $\hat{\mathbf{H}}|n\rangle = \epsilon_n|n\rangle$. For a system in thermal equilibrium $\hat{\rho}_T = \exp(-\beta\hat{\mathbf{H}})/Z$, the energy entropy is proportional to the thermodynamical entropy $\sigma_E = k_B(\log Z + \beta\langle\hat{\mathbf{H}}\rangle)$ where Z is the partition function.

Since the entropy is related to the observable measured, the observable which minimizes this entropy defines an invariant of the system. The minimization leads to an observable represented by an operator which commutes with $\hat{\rho}$. The entropy related to the minimum dispersion observable defines the von-Neumann entropy:[28]

$$\sigma_{vn} = -tr\{\hat{\rho}\log\hat{\rho}\} = -\langle\log\hat{\rho}\rangle, \tag{2.2}$$

Obviously $\sigma_{vn} \leqslant \sigma_E$, with equality for a thermal ensemble. Cooling means that the dispersion of the system is reduced. In the extreme pure state the von Neumann entropy becomes zero, and a pure energy eigenstate will have zero energy entropy.

It is important to examine the relation between the entropy of the complete system and its partitions. For example partitioning the system to the ground and excited electronic manifolds results in[7]

$$\sigma_{vn} \leqslant \sigma_{vn}(g) + \sigma_{vn}(e) = \overline{\sigma_{vn}}(g) + \overline{\sigma_{vn}}(e) + S_{mix} \tag{2.3}$$

where $\sigma_{vn}(g/e) = tr\{\hat{\rho}_{g/e}\log\hat{\rho}_{g/e}\}$, $\overline{\sigma_{vn}}(g/e) = tr\{\overline{\rho_{g/e}}\log\overline{\rho_{g/e}}\}$, $p_{g/e} = \langle\hat{\mathbf{P}}_{\mathbf{g/e}}\rangle$ and $S_{\mathrm{mix}} = -p_g\log p_g - p_e\log p_e$. Equality in Eq. (2.3) results only when $\hat{\rho}_c = 0$. The inequality is the result of the restriction due to the partition to the limited set of operators used to characterize the system: $\hat{\mathbf{O}} = \hat{\mathbf{P}}_\mathbf{g}\otimes\hat{\mathbf{A}}_\mathbf{g} + \hat{\mathbf{P}}_\mathbf{e}\otimes\hat{\mathbf{B}}_\mathbf{e}$. Notice that $\sigma_{vn}(g/e)$ relate to the unnormalized density operator and are therefore extensive while $\overline{\sigma_{vn}}(g/e)$ relate to the normalized density operator and are therefore intensive. For an open quantum system the intensive entropy $\overline{\sigma_{vn}}(g)$ provides a measure of the single particle cooling. However, the extensive entropy, $\sigma_{vn}(g)$, does not provide a good measure of the cooling achievement since the number of particles (p_g) can shrink to zero due to evaporation to the excited state, and thus this entropy can decrease without any cooling per se. For this reason it is useful to consider the Renyi entropy:[29]

$$\sigma_R = tr\{\hat{\rho}^2\} = \langle\hat{\rho}\rangle. \tag{2.4}$$

The Renyi entropy is a concave function which maximizes at one for a pure state and vanishes when all population is lost. For the Renyi entropy a similar partitioning inequality can be derived: $\sigma_R \geqslant \sigma_R(g) + \sigma_R(e) = p_g^2\overline{\sigma_R}(g) + p_e^2\overline{\sigma_R}(e)$ where $\sigma_R(g/e) = tr\{\rho_{g/e}^2\}$ and $\overline{\sigma_R}(g/e) = tr\{\overline{\rho_{g/e}^2}\}$. Equality is attained only when there is no coherence between the ground and excited surface.

The extensive Renyi entropy $\overline{\sigma_R}(g)$ has several advantages over the extensive von Neumann definition as a measure of cooling achievement. The Renyi entropy increases both as the degree of purity of a state increases, as well as when the amount of population in that state increases. This is in contrast with the extensive von Neumann definition of the entropy, in which the entropy on the ground state can be *decreased* (note that the sign of the Renyi entropy is reversed relative to the von Neumann definition) either by genuine cooling or by evaporation of particles, i.e. transfer to the excited electronic state. One of the most exciting applications of cooling is achievement of Bose condensation. Evaporation of hot particles is of no value per se for Bose condensation, since there is no increase in $p_{\max}$, the maximum population in any level. Thus, one can make the claim that the increase in the extensive Renyi entropy provides a direct measure of the approach to Bose condensation in a way that the decrease in the extensive von Neumann entropy does not.

Another way to express this is in terms of phase space. An increase in the extensive Renyi entropy corresponds to an increase in phase space density of the system, whether there is change of particle number (i.e. transfer of population to the excited electronic state) or not. In contrast, a decrease in the extensive von Neumann entropy is a measure of an increase in phase space density only if there is no evaporation. The extensive von Neumann entropy can be reduced by evaporating the population in the higher energy vibrational levels; however, there will be no accompanying change in phase space density, The Renyi entropy takes into account the inequivalence between evaporating high energy components and true increase in phase space density. Again, increase in phase space density is closely related to the approach to Bose condensation.

A third perspective is obtained by noting that for normalized $\hat{\rho}$, $(tr\{\hat{\rho}\} = 1)$, $tr\{\hat{\rho}_g^2\} \leqslant tr\{\hat{\rho}^2\} \leqslant 1$, where the equality is satisfied if and only if $\hat{\rho} = \hat{\rho}_g$ is a pure state. Thus, the Renyi entropy is a direct measure of the degree of coherence,[30] i.e. approach to pure state character in the system. In retrospect, this is a very natural measure of Bose condensation, in which all particles go into the same pure state (which need not necessarily be the ground state of the system, or even an eigenstate). Although in this paper we focus on single particle cooling (i.e. quantum statistics is not considered) it seems the Renyi entropy is better suited for describing the quantum statistical domain. Recall that the usual logarithmic functionality in the Gibbs-von Neumann definition is designed to give extensive behavior, i.e. linear proportionality between entropy and system size. When quantum statistics are important and coherence extends over a large fraction of the system volume it is not clear that the conventional property of extensive behavior remains meaningful.

We turn now to the partitioning of the system into the

primary and bath degrees of freedom. This leads to the inequality:

$$\sigma_{vn} \leqslant -\langle \log\hat{\rho}_s \rangle - \langle \log\hat{\rho}_b \rangle - I_{s,b} = \sigma_{vn}(s) + \sigma_{vn}(b) - I_{s,b}, \tag{2.5}$$

where $I_{s,b}$ is the maximal mutual information between the system s and the bath b as measured by a coincidence experiment. This inequality has been proved by Lindblad[8] and is a quantum effect imposed by restricting the observables to the two parts. Equality in Eq. (2.5) is obtained when the correlation between the system and the bath can be characterized by the operator $\hat{\mathbf{C}} = \hat{\mathbf{A}}_\mathbf{s} \otimes \hat{\mathbf{B}}_\mathbf{b}$. When there is no correlation between the system and bath $\hat{\rho} = \hat{\rho}_s \otimes \hat{\rho}_b$, then $I_{s,b} = 0$.

With these definitions cooling can be viewed in a number of alternative ways. From an intensive viewpoint as:

- a reduction of the average energy $tr\{\mathbf{H}\overline{\rho_g}\}$,
- a reduction of entropy σ_E associated with energy dispersion,
- a reduction of intensive von Neumann entropy $\overline{\sigma_{vn}}(g)$,
- an increase of the intensive Renyi entropy $\overline{\sigma_R}(g)$.

From an extensive viewpoint:

- an increase in the ground state number density, $\langle \hat{\mathbf{P}}_\mathbf{0} \rangle$ where $\hat{\mathbf{P}}_\mathbf{0} = |0\rangle\langle 0|$,
- an increase in the extensive Renyi entropy $\sigma_R(g)$.

B. Limitations imposed by unitary transformations

In the finite system under study the dynamics is described by a unitary evolution operator. Under these conditions the total von Neumann entropy or the Renyi entropy are preserved. The conservation of these two entropies forms a special case of a general theorem that the expectation of a function of $\hat{\rho}$ i.e. $\langle f(\hat{\rho}) \rangle$ is invariant under unitary transformation. The proof is based on the cyclic invariance of the trace and the fact that $\hat{\rho}$ and $f(\hat{\rho})$ commute.[31] Therefore, *in a cooling process generated by a unitary evolution, the decrease in entropy in the primary system is compensated for by an increase in the remainder*.

There is a simple geometrical interpretation to the constancy of the Renyi entropy under unitary evolution. In a two level system the density operator can be represented as a three component of a Bloch-type vector in which the z-component is the population difference between the two levels, and the x and y components are the real and imaginary parts of the polarization of the state. The length of the vector is equal to $tr\{\hat{\rho}^2\}$. In the absence of dissipation, the vector precesses around the instantaneous field vector without changing length. For a pure state, the vector evolves such that the tip is always on the unit sphere, while for an impure state the tip evolves on a sphere of constant, smaller radius.

Another viewpoint concerning unitary transformations is that they preserve the eigenvalues of the density operator. This leads to a further consequence that, starting from a thermal state, the projection on the ground state $\langle \hat{\mathbf{P}}_\mathbf{0} \rangle$ cannot exceed the initial projection in the thermal state.[32] The proof for the latter is as follows. Let $\hat{\rho}(t) = \hat{\mathbf{U}}\hat{\rho}_T\hat{\mathbf{U}}^\dagger$ where $(\rho_T)_{ij} = \exp(-\beta E_j)\delta_{ij}/Z$ is diagonal. Then

$$(\rho(t))_{ii} = \sum_{jk} U_{ij}(\rho_T)_{jk}U^\dagger_{ki} = \sum_j U_{ij}U^\dagger_{ji}(\rho_T)_{jj} = \sum_j |U_{ij}|^2(\rho_T)_{jj}. \tag{2.6}$$

Now, the maximum value of $(\rho(t))_{ii}$ is obtained if $U_{ij} = 1$ when j is the index for the maximum eigenvalue of ρ_T and $U_{ij} = 0$ otherwise. Hence, $(\rho(t))_{ii} \leqslant (\rho_T)_{\max}$.

It is worth noting that this same constraint holds even if part of the system is projected out. For example, one of the applications presented below involves the use of an excited electronic state to promote cooling in the ground electronic state. In principle, this excited state population can be separated from the ground state population in the lab, e.g. by ionization followed by ion optics. Hence the projector can be realized in the lab. Such a projection cannot, however, assist in increasing the maximum eigenvalue. The proof is as follows:

$$\hat{\rho}(t) = \hat{\mathbf{U}}_\mathbf{2}\hat{\mathbf{P}}\hat{\mathbf{U}}_\mathbf{1}\hat{\rho}_T\hat{\mathbf{U}}_\mathbf{1}^\dagger\hat{\mathbf{P}}\hat{\mathbf{U}}_\mathbf{2}^\dagger, \tag{2.7}$$

$$(\rho(t))_{ii} = \sum_{jk} V_{ij}(\rho_T)_{jk}V^\dagger_{ki} = \sum_j V_{ij}V^\dagger_{ji}(\rho_T)_{jj} = \sum_j |V_{ij}|^2(\rho_T)_{jj}, \tag{2.8}$$

where $\hat{\mathbf{V}} = \hat{\mathbf{U}}_\mathbf{2}\hat{\mathbf{P}}\hat{\mathbf{U}}_\mathbf{1}$. Note that $\mathbf{V}$ is no longer unitary. However, since the effect of $\hat{\mathbf{P}}$ is to set certain rows of U_1 equal to zero, it is clear that if the maximum value of $\Sigma_j|U_{ij}|^2$ is 1, then the maximum value of $\Sigma_j|V_{ij}|^2$ is also equal to 1. Consider now an initial thermal state on the ground electronic surface. It becomes clear that under a unitary evolution the maximum goal obtainable is to evaporate all other eigenstates except the ground state.

Similarly, a unitary transformation can only increase the average energy when the initial state is in a thermal distribution. The proof follows from the observation that the eigenvalues of $\hat{\rho}$ can change position but cannot change magnitude under a unitary transformation. At $t = 0$ $tr\{\hat{\rho}_T\hat{\mathbf{H}}\} = Z^{-1}\Sigma_n e^{-\beta E_n}E_n$. The eigenvalues of $\hat{\rho}_T$ are ordered monotonically, and thus any permutation of these eigenvalues via a unitary transformation gives additional weight to higher values of E_n, increasing the average energy.

C. Optimal control of laser cooling

The agents of change are unitary transformations generated by a time dependent Hamiltonian. This Hamiltonian is

controlled by the external electromagnetic field. Considering cooling to be the objective there is infinite leverage in constructing a field leading to this objective. Optimal control theory is employed to find the optimal unitary transformation with the objective of cooling, subject to the constraints of finite duration and a limited field power.[20,33,34]

Within the present quantum mechanical context, the objective is represented as a target operator $\hat{\mathbf{A}}$ obtained in a finite time interval $\{0,t_f\}$. Optimal control theory (OCT) seeks the optimal field as a variation problem of an objective J which is a functional of the field $\epsilon(t)$:

$$J=tr\{\hat{\rho}(t_f)\hat{\mathbf{A}}\}. \tag{2.9}$$

Two constraints are imposed:

(1) The evolution of the system has to be governed by the Liouville-von Neumann equation.
(2) The total field energy has to be minimized.

These two constraints lead to the modified objective

$$\overline{J}=tr\{\hat{\mathbf{A}}\hat{\rho}(t_f)\}-\int_0^{t_f} tr\left\{\left(\frac{\partial\hat{\rho}}{\partial t}-\mathscr{L}(\hat{\boldsymbol{\rho}})\right)\hat{\mathbf{B}}\right\}dt$$

$$-\lambda\int_0^{t_f}|\epsilon|^2dt. \tag{2.10}$$

$\hat{\mathbf{B}}$ is an operator Lagrange multiplier and λ is a scalar Lagrange multiplier. An extremum for the objective J has to be found. It is done by a variation of J with respect to $\delta\hat{\rho}$, δ Real(ϵ) and δ Imag(ϵ). The variation leads to the following equations of motion:

$$\frac{\partial\hat{\rho}}{\partial t}=\mathscr{L}(\hat{\rho}), \tag{2.11}$$

$$\frac{\partial\hat{\mathbf{B}}}{\partial t}=-\mathscr{L}^{+}(\hat{\mathbf{B}}), \tag{2.12}$$

and to the final condition for the Lagrange multiplier $\hat{\mathbf{B}}$:

$$\hat{\mathbf{B}}(t_f)=\hat{\mathbf{A}}. \tag{2.13}$$

The structure of the above equations represents two counter currents, where the density operator $\hat{\rho}$ carries the information from the initial state $\hat{\rho}(0)$ forward in time and the target operator $\hat{\mathbf{B}}$ propagates the information on the objective $\hat{\mathbf{A}}$ backward in time. The difficulty in solving these equations is the result of the temporal separation in the boundary conditions and of the nonlinear dependence of the optimization objective on the field. In the previous study, an instantaneous approach was employed to approximate the optimal solution based on a monotonic improvement of the objective. In the present study a global iterative approach is employed based on Krotov's method.[35] The details of the method are found in Appendix A. In all cases studied, the global approach outperformed the local method significantly. As a result the unitary transformation obtained is very close to the optimal cooling achievement subject to the constraints imposed. This means that the particular solutions obtained are typical which allows one to draw general conclusions.

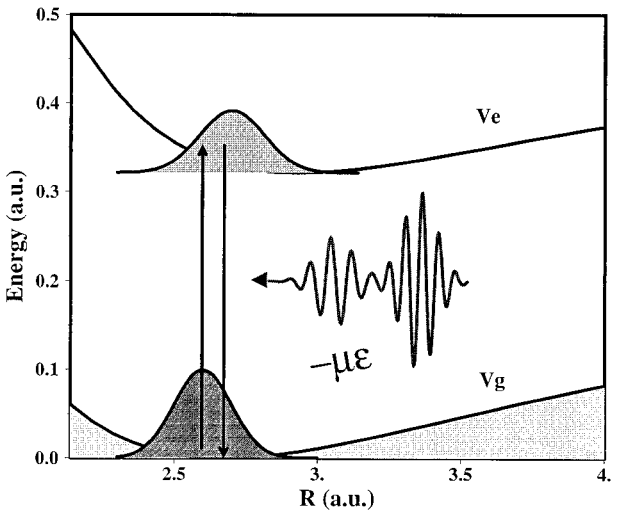

FIG. 1. Schematic cooling model based on the HBr molecule. The ground and excited potential energy surfaces are shown together with the wavefunctions. The transitions induced by the radiation field, the agents of control are also indicated.

III. APPLICATIONS

The object of control is to cool a particular vibrational mode on the ground electronic surface. The time duration allowed for the process is ten vibrational periods. The short duration classifies the process to be in the impulsive limit. The radiation field couples the ground electronic surface by a transition dipole to an excited electronic surface. When the radiation is turned off the coupling between the different parts of the system vanishes (Eq. (1.6)).

The first system studied is constructed from a single vibrational mode and is identical to the system of Ref. 7. Fig. 1 shows the model. Initially the upper electronic manifold is not populated. In the one mode study the radiation populates the excited electronic surface creating an entropy sink. In the second system studied, additional vibrational modes serve as an entropy sink, and the excited surface population can be regained.

A. Reexamination of the Results of Paper I: Electronic entropy sink

The system studied is modeled on the HBr molecule. The initial state is thermal with a temperature of 5000 K located exclusively on the ground electronic surface. In the instantaneous control approach,[7] the cooling scenario is divided into two stages. In the first stage, an initial short pulse moves the population to the excited electronic surface, which acts as an entropy sink. In the second stage, the ground surface population is cooled at the expense of heating the excited surface population. The amount of population transfered to the excited surface is set by the first pulse and from then on kept constant. Instantaneous control of energy transport between the surfaces was brought about with zero additional population transfer. The results of the calculations show a small amount of intensive cooling on the ground electronic surface.

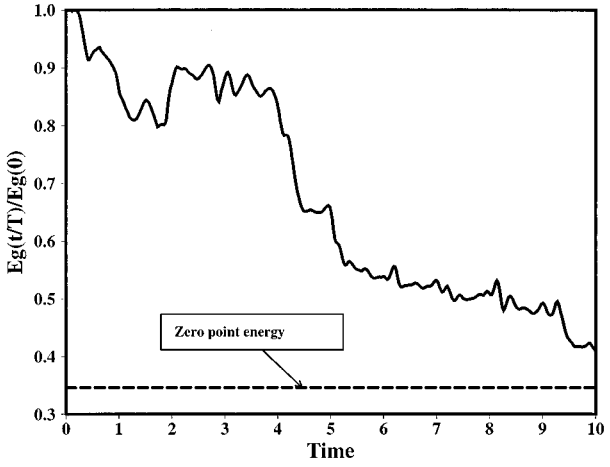

FIG. 2. Ground surface intensive energy as a function of time. The time is in units of vibrational periods on the ground electronic surface. ($E_g(0)=1.7210^{-2}$ a.u.)

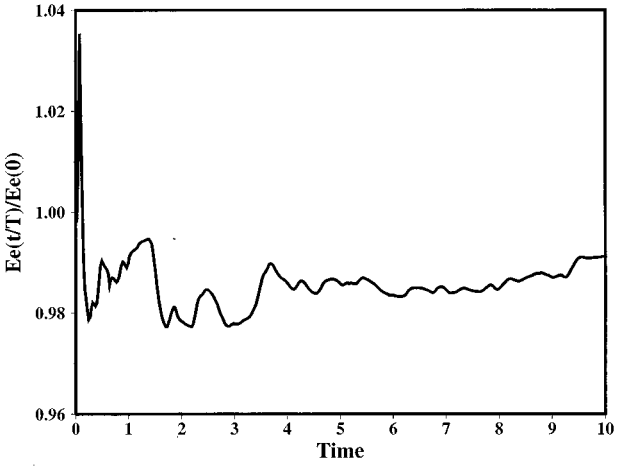

FIG. 3. Excited surface intensive energy as a function of time.

This cooling scenario has been reconsidered in the present study, employing optimal control theory. An objective operator residing on the ground electronic surface was chosen to maximize the projection on the zero eigenstate and minimize the projection on all other eigenstates:

$$\hat{\mathbf{A}}=\left(|0\rangle\langle 0|-\sum_{n=1}^{\infty}|n\rangle\langle n|\right)\otimes\hat{\mathbf{P}}_{\mathbf{g}}. \tag{3.1}$$

The population transfer to the excited surface was unlimited in contrast to the instantaneous control approach.

The results of the calculation are presented in Fig. 2. Significant intensive cooling is observed, reaching very close to a pure state on the ground electronic surface in the target time of ten periods.

The difference between the global and instantaneous approach is noticed in Fig. 2, showing that in the global approach the reduction in the ground surface energy is not monotonic. The final ground surface energy is $E_g(t_f)=0.408$ which is quite close to the zero point energy 0.346.

On the excited surface the intensive energy is approximately constant as seen in Fig. 3. The initial spike is insignificant since the excited state population is negligible at that point.

The projected population on the ground surface $\langle\hat{\mathbf{P}}_{\mathbf{g}}\rangle$ in Fig. 4 shows the difference from the instantaneous control approach. The trend is for a significant population reduction.

The target of cooling can also be viewed as a decrease in entropy. Fig. 5 shows the entropy reduction. By coarse-graining the time scale to units of a vibrational period the entropy decrease can be considered monotonic. The conclusion from Fig. 5 is that the three types of intensive entropy are qualitatively very similar. The similarity between the von Neumann entropy and the energy entropy means that the cooling process is very close to adiabatic i.e. the system is very close to diagonal in the energy representation. The total entropy reduction is a factor of 10.

On the excited surface the entropy fluctuates considerably (Fig. 6) with a very large deviation between the energy and von Neumann entropies. This reflects the fact that the projected state on the excited surface is nonstationary.

The entropy picture is summarized in Fig. 7 where the restricted von Neumann entropy (Eq. 2.3) is compared to the total entropy which is constant. The very large increase in the restricted entropy reflects the buildup of significant electronic coherence. This coherence is responsible for a nonzero transition dipole expectation $\langle\hat{\mu}\otimes\hat{\mathbf{S}}_{+}\rangle$ which is the primary quantity which enables control. When the restricted von Neumann entropy is identical to the total von Neumann entropy the correlation between the ground and excited electronic manifolds vanishes, thus the ability to control is lost. The final approach of the restricted entropy to the initial entropy value reflects the achievement of the cooling objective where all the initial ground surface entropy is transferred to the excited surface. At the target time the ground surface approaches a pure state which means that the rate of cooling or energy decrease, vanishes.[7]

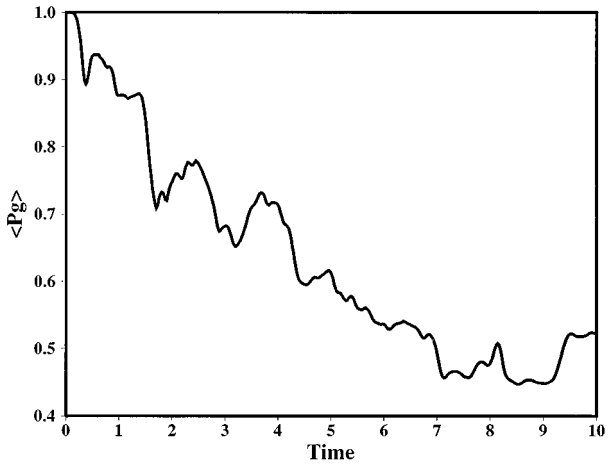

FIG. 4. Ground surface population as a function of time.

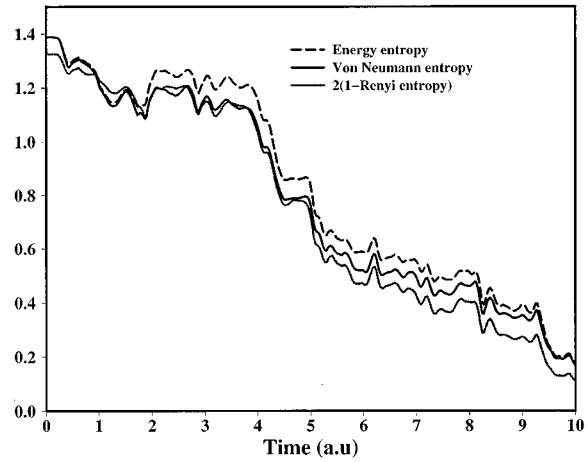

FIG. 5. Ground surface intensive entropy as a function of time. von Neumann entropy $\overline{\sigma_{vn}}(g)$ (solid line), energy entropy $\overline{\sigma_E}(g)$ (dashed line) and $2(1-\overline{\sigma_R}(g))$ (dotted line).

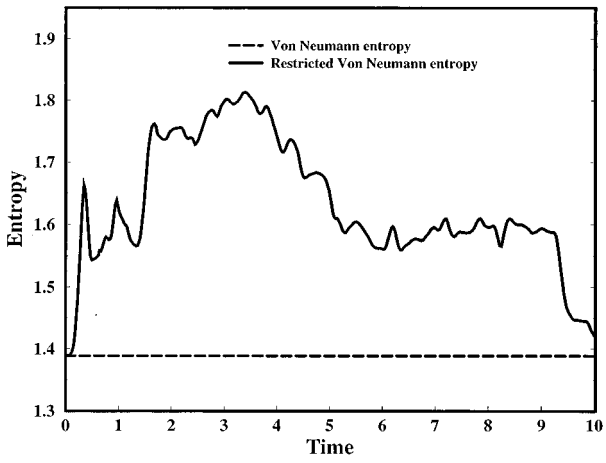

FIG. 7. von Neumann entropy of the full density operator σ_{vn} (dashed line) and the restricted von Neumann entropy to two surfaces $\sigma_{vn}(g)+\sigma_{vn}(e)$ (solid line) as a function of time.

At this point the cooling scenario should be analyzed from an extensive point of view. Fig. 8 shows the difference between the intensive and extensive Renyi entropies. A clear decrease in the extensive Renyi entropy is observed indicating that the cooling is at the expense of the ground surface population i.e. evaporative cooling.

A similar picture is obtained by examining the phase space distribution function in Fig. 9. The final distribution is more compact than the initial one. This result is at the expense of a smaller volume under the distribution peak. On the excited surface the rough landscape represents a nonstationary state.

Examining the cooling achievement from an extensive point of view shows that the maximum cooling obtainable is limited by the conservation of eigenvalues of the density operator. Therefore it cannot exceed the evaporative cooling limit. This can be seen in Fig. 10 where both the instantaneous and global optimization results are shown. Fig. 10 shows the limitations imposed on the cooling achievement by the unitary transformation. In the initial state the eigenvalues are distributed according to the thermal population on the different vibrational levels of the ground electronic surface showing a monotonic decrease. In the instantaneous optimization after the excitation pulse the eigenvalues on the ground surface decrease due to population transfer to the excited surface. The cooling process increases the lowest eigenvalues on ground surface density and further decreases the rest. The increase in the $v=0$ eigenvalue only reaches its initial value. In the global optimization the evaporation of all the higher eigenstates is clearly visible.

Summarizing, in the optimal control cooling process the final result is evaporative cooling, and the extensive Renyi entropy will hence decrease. The rate of the process is extremely fast: within ten vibrational periods all higher vibrational eigenvalues have been removed to the excited elec-

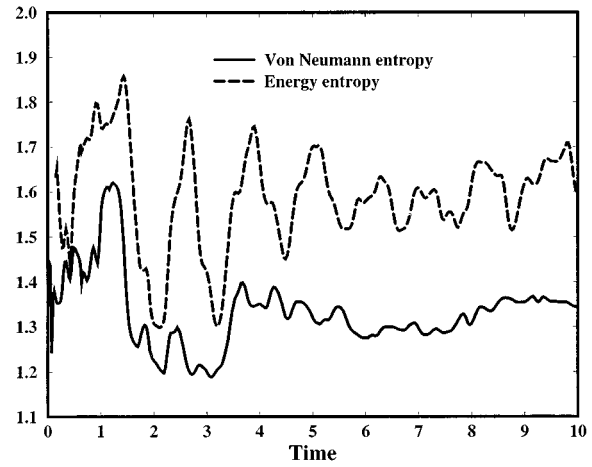

FIG. 6. Excited surface intensive entropy as a function of time. von Neumann entropy (solid line) and energy entropy (dashed line).

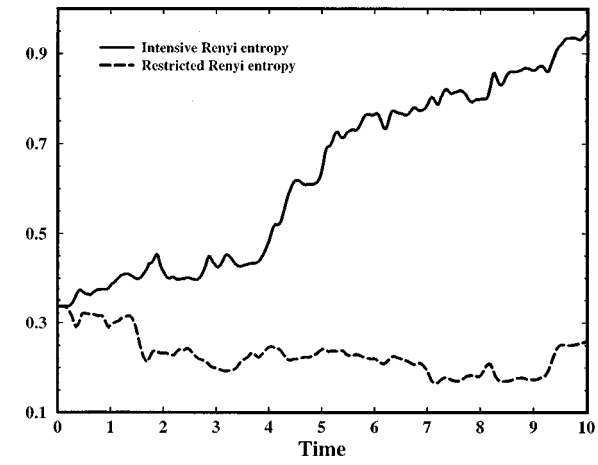

FIG. 8. Ground surface intensive Renyi entropy $\overline{\sigma_R}(g)$ (solid line) and ground surface extensive Renyi entropy $\sigma_R(g)$ (dashed line) as a function of time.

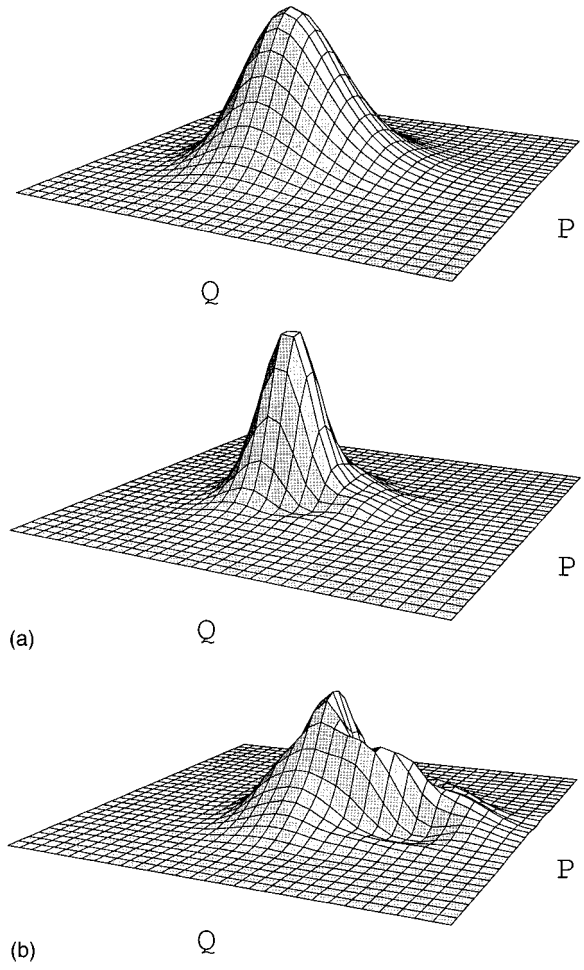

FIG. 9. Coordinate-momentum phase space Wigner distribution function of: (a) initial thermal state $\hat{\mathbf{W}}_g(q,p,0)$. (b) Ground surface final state $\hat{\mathbf{W}}_g(q,p,t_f)$. c) Excited surface final state $\hat{\mathbf{W}}_e(q,p,t_f)$.

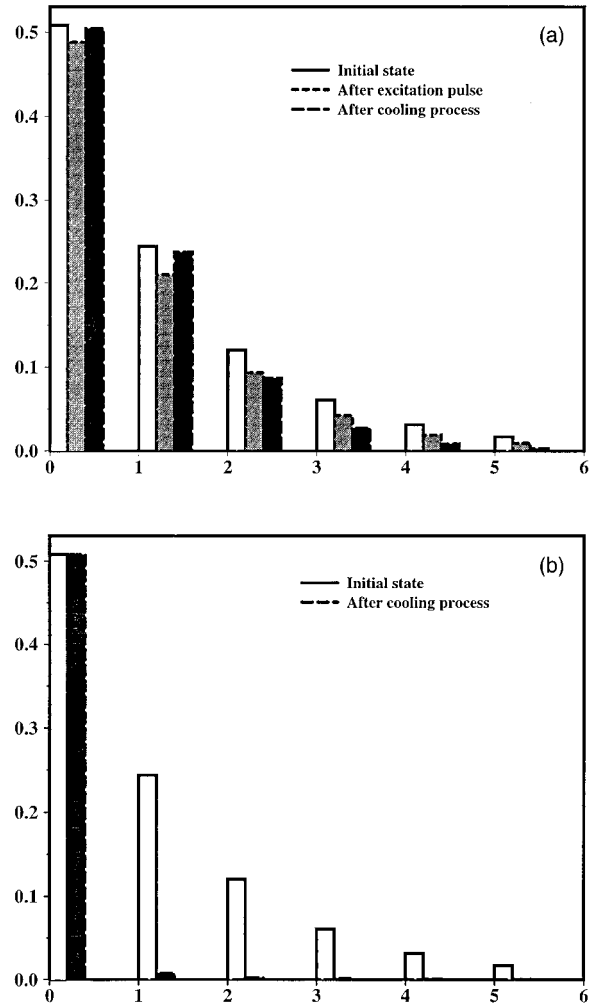

FIG. 10. Eigenvalues of the ground surface density operator: (a) Three stages in the instantaneous optimization. *i*. The initial thermal state (white), *ii*. after the excitation pulse (gray), *iii*. after the cooling process (dark). (b) Two stages in the global optimization. *i*. initial thermal state (white), *ii*. at the final time t_f (dark).

tronic surface. The optimal control mechanism evaporates the excited vibrational eigenstates without disturbing the lower ones. As a result the process seems adiabatic on the ground electronic surface but impulsive on the excited surface.

B. Vibrational entropy sink

To overcome the limitations imposed by the conservation of eigenstates under unitary transformations a vibrational mode is added which serves as the entropy sink. In this construction, the primary mode is embedded in a larger system. The cooling model employed consists of two vibrational modes demonstrated in Fig. 11. The x mode serves as the primary mode with an harmonic potential of frequency $\omega_x=1$. The y mode is the bath mode with frequency $\omega_y=0.5$. The origins of the excited surface modes were shifted in relation to the ground surface. The coupling between the modes is induced by the transition dipole function with the nuclear component $\hat{\mu}=\overline{\mu}(\hat{\mathbf{x}}+\hat{\mathbf{y}})$. With this choice the coupling between modes depends strongly on the field intensity. The coupling vanishes at least quadratically when the field turns off.

The initial state is constructed as a direct product state of the primary and sink vibrational modes exclusively on the ground electronic surface. In each vibrational mode a mixture of the $v=0$ and $v=1$ states was constructed:

$$\hat{\rho}_i=\frac{1}{4}((|0_x\rangle\langle 0_x|+|1_x\rangle\langle 1_x|)\otimes(|0_y\rangle\langle 0_y|+|1_y\rangle\langle 1_y|))\otimes\hat{\mathbf{P}}_\mathbf{g}. \tag{3.2}$$

This initial state has equal entropy in the primary and bath mode, with zero correlation $\sigma=\sigma_x+\sigma_y$, $\sigma_i=\log 2$.

Optimal control theory was employed to seek a cooling mechanism. The objective operator in the primary x mode consists of the projection on the ground surface, $\hat{\mathbf{A}}_\mathbf{x}=(|0\rangle\times\langle 0|)\otimes\hat{\mathbf{P}}_\mathbf{g}$, and the identity operator in the y mode:

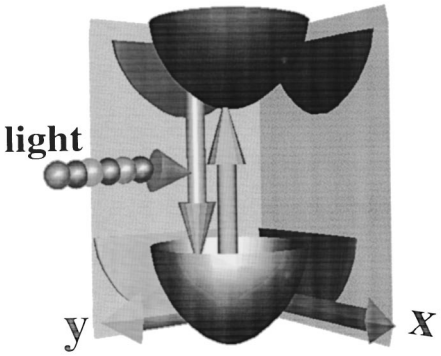

FIG. 11. Schematic cooling model for the two-mode model. The x mode is the primary mode. The y mode is the entropy sink. The light induces population and energy transitions from the ground to the excited surface and vise versa. Energy can flow from one mode to the other through the excited electronic surface. The system can be partitioned to the ground and excited electronic manifolds and/or the x and y vibrational modes. The reduced description of the primary and bath modes is shown as the projections on the perpendicular one dimensional planes.

$\hat{\mathbf{A}}=\hat{\mathbf{A}}_x\otimes\hat{\mathbf{I}}_y$. Again the time duration is limited to ten vibrational periods. The performance of the intensive energy reduction is shown in Fig. 12.

From Fig. 12 it is clear that the energy in the primary mode is reduced almost to the zero point value ($E_x(g)=0.525$ compared to 0.5). The energy in the bath mode more than compensates this decrease, due to absorption of energy from the field. At intermediate times the energy is stored on the excited electronic surface. This is in accordance with Fig. 13 showing significant population transfer to the excited surface during the cooling process.

In the first five cycles it seems that the energy reduction in the primary mode is due to population transfer to the excited electronic surface. During the last five cycles this energy is pumped to the bath mode. Fig. 14 shows the entropy balance of the cooling process.

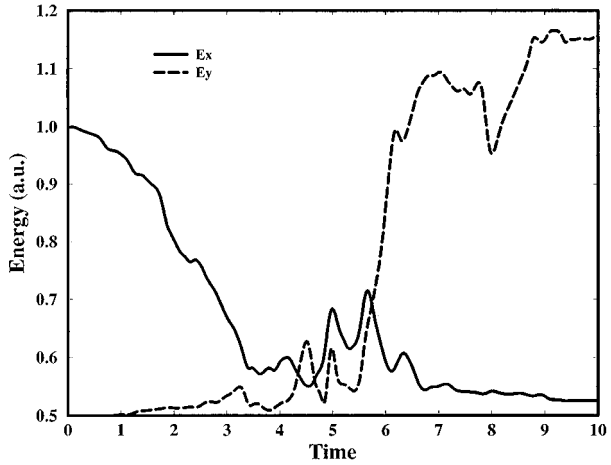

FIG. 12. Intensive energy in the primary E_x mode on the ground electronic surface and in the bath mode E_y. The time is in vibrational periods of the x mode. The frequencies of the modes are $\omega_x=1$ and $\omega_y=0.5$.

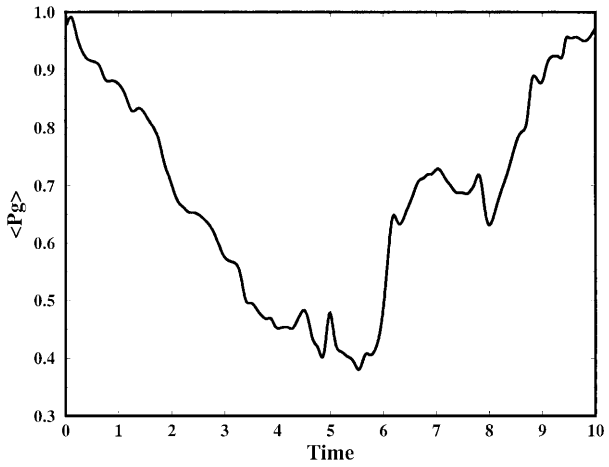

FIG. 13. Ground surface population as a function of time. The time is in vibrational periods of the x coordinate on ground surface.

The entropy decrease on ground surface of the primary x mode is observed, which is the finger print of intensive cooling. The entropy reduction is by approximately a factor of 10. The total entropy on x mode shows that an appreciable portion is due to amplitude on the excited surface. The y mode entropy compensates for the decrease in the x ground surface.

Fig. 15 proves that this cooling is also extensive. The increase in the ground surface density and in the extensive Renyi entropy signify this fact. The extensive Renyi entropy $\sigma_R(g)$ decreases in the first five vibrational periods meaning that this part of the process is evaporative. In the last part of the process the $\sigma_R(g)$ and the number density increase be-

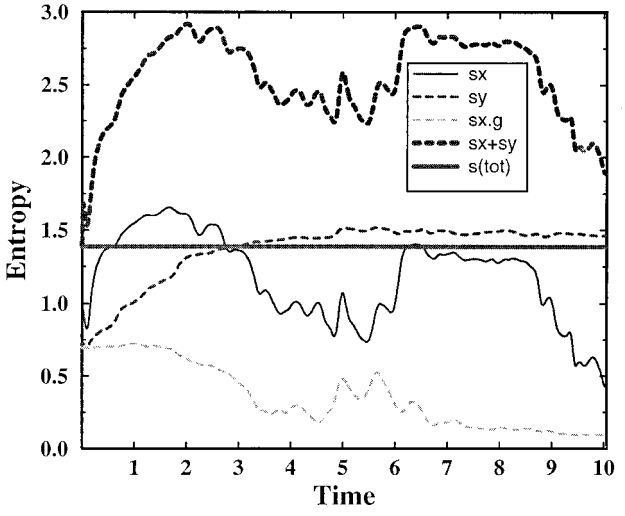

FIG. 14. Entropy balance of the two mode cooling process showing the total entropy which is conserved. The ground surface von Neumann intensive entropy $\overline{\sigma_{vn}}(g)_x$ as a function of time. The total entropy of the x mode: $(\overline{\sigma_{vn}})_x$, The total entropy of the y mode: $(\overline{\sigma_{vn}})_y$, and the sum of the entropy of the two modes.

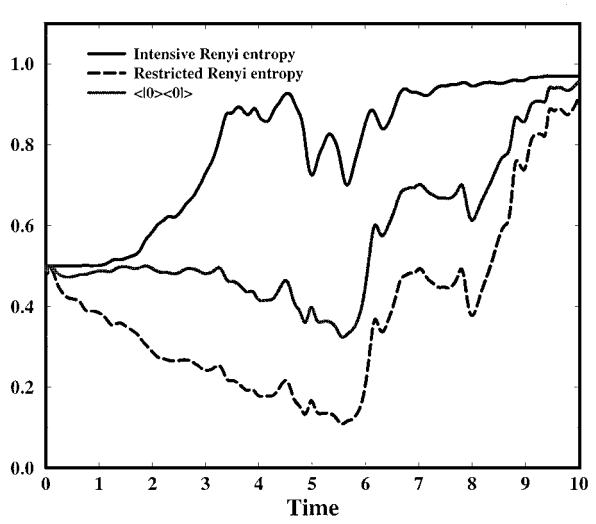

FIG. 15. Intensive Renyi entropy $\overline{\sigma_R}(g)$ (solid line), extensive Renyi entropy $\sigma_R(g)$ (dashed line) and the expectation of projection $\hat{\mathbf{I}}_y \otimes |0_x\rangle\langle 0_x|$ on the zero vibrational level (gray) of the ground surface reduced density $tr_y\{\hat{\rho}_g\}$ as a function of time.

yond their initial value meaning that extensive cooling is obtained.

The optimal field is shown in Fig. 16. It shows some pulse structure with a very broad frequency spectrum.

The probability density of the initial and final states on the x and y coordinates is shown in Fig. 17. The cooling process can be viewed as rearranging the ''mountains'' such that the profile in the x mode becomes narrow while maintaining the total volume.

Finally Fig. 18 shows the phase space distribution of the primary mode before and after the cooling process. The final state is very close to the ground vibrational state of this oscillator.

It is clear from this study that both intensive as well as extensive cooling of the primary mode has been obtained.

The instantaneous optimization approach was also used for cooling the two mode system. First it was tried for the initial state

$$\hat{\rho}_0 = \frac{1}{2}(|0_x 0_y\rangle\langle 0_x 0_y| + |1_x 0_y\rangle\langle 1_x 0_y|). \tag{3.3}$$

The entropy of this state is log2 in the primary mode and zero in the bath mode meaning that system is hot and the bath cold. The instantaneous optimization solution was able to remove 98.6% of the excess energy from the primary mode within 21 vibrational periods. The global optimization was superior, it removed 99.7% of the excess energy in 10 vibrational periods. When the instantaneous optimization was applied to the initial state Eq. (3.2) with a hot initial bath the cooling rate was extremely slow. Nevertheless the projection on the ground vibrational level exceeded its initial value.

In the instantaneous approach the local target was defined as: primary mode energy reduction, subject to zero population transfer between the ground and excited electronic surfaces. Renyi entropy increase was also used as a target showing comparable cooling achievement.

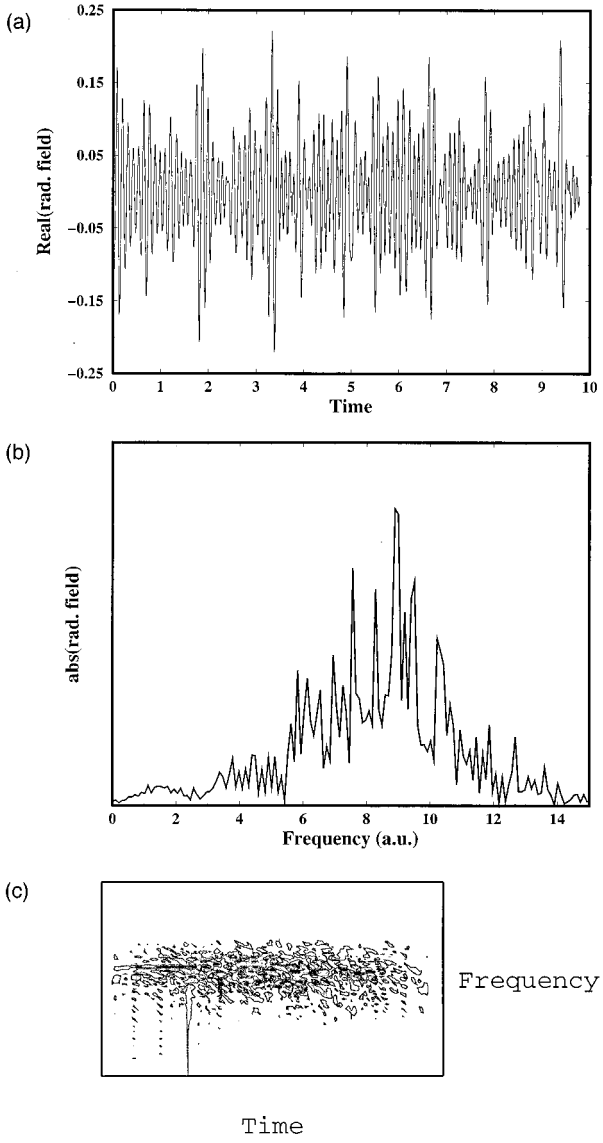

FIG. 16. (a) Real part of the radiation field as a function of time as obtained from the global optimization for cooling the ground surface vibrational motion. The time is in units of vibrational period on the ground surface. (b) Spectrum of the field shown in (a). (c) Time - energy phase space Wigner distribution of the field.

IV. DISCUSSION AND SPECULATION

There are two basic cooling strategies: evaporation and the heat pump mechanism. With the use of optimal control theory these strategies can be cast into the realm of impulsive cooling of molecular vibrations. For a single mode system the only possibility is evaporative cooling which in its most extreme application means evaporating all levels except the ground vibrational level. Analysis has shows that such a strategy exploiting the excited electronic surface as the evaporative sink is possible in finite time. If there is unlimited time, a sequence of adiabatic passage processes[36,37] can be imagined which moves all the ground electronic surface

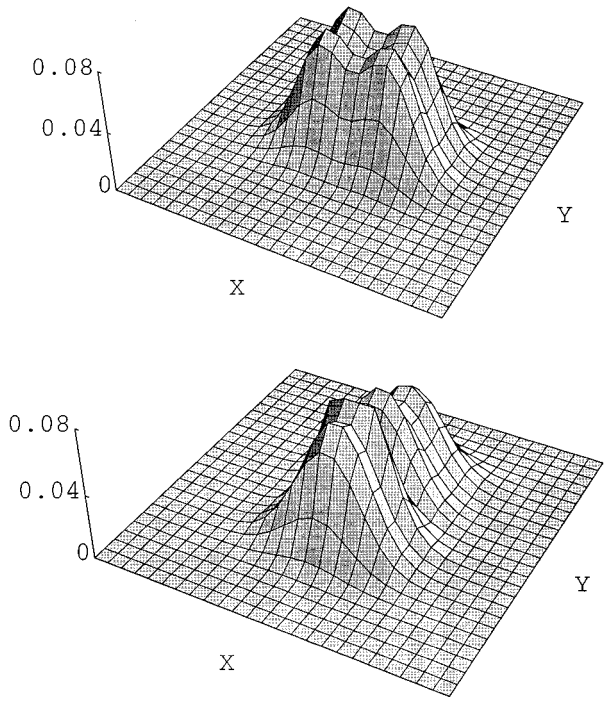

FIG. 17. Diagonal elements of the density operator on the ground electronic surface $\hat{\rho}_g(x,x,y,y)$. a) Initial state, and b) final state.

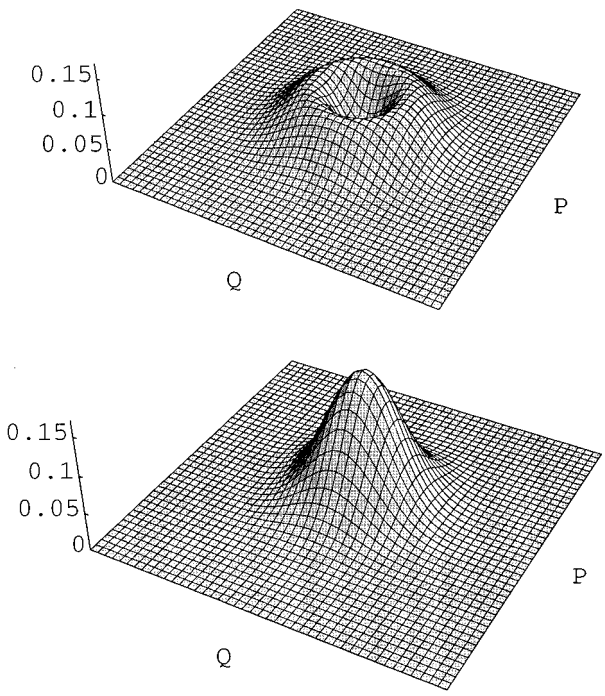

FIG. 18. Coordinate - momentum phase space Wigner distribution of the reduced density on x primary mode. (a) Initial state, and (b) final state.

excited vibrational levels to the upper electronic manifold. The selectivity of this process depends on the time duration allocated. The minimum energy input for such a process can be obtained by ordering each reactant and target vibrational level according to increasing energy. The finite time optimal control solution is less efficient in energy consumption, but maintains the selectivity property. The reduced efficiency is manifested in the final state on the excited surface $\hat{\rho}_e$, which is nonstationary meaning there is a higher energy content. For a time duration of ten cycles the energy price is quite small.

The obvious drawback of the evaporative cooling strategy is the inability to increase the number density of the ground state beyond its initial value. The role of radiation in this process is to access the entropy sink by moving population to the excited surface. In synchronization with this task electronic coherence is established $\hat{\rho}_c \neq 0$. This electronic coherence is a necessary requirement for controllability.

Cooling by a heat pump mechanism is superior to evaporative cooling since it does not sacrifice the number density to obtain the cooling goal. Embedding the primary system in even one bath mode is sufficient for a heat pump mechanism to be operative. This construction in which the primary system is embedded into a larger system overcomes the limitation imposed by unitary transformations.

There are advantages to using the Renyi entropy to characterize the degree of cooling of a system. An increase in Renyi entropy corresponds to an increase in phase space density of the system, whether there is change of particle number (i.e. transfer of population to the excited electronic state) or not. Yet, evaporation is of no value for Bose condensation, since there is no increase in the $p_{\max}$, the maximum population in any level. Thus, one can make the claim that the increase in the Renyi entropy provides a direct measure of the approach to Bose condensation in a way that the decrease in the (extensive) von Neumann entropy does not. Moreover, the Renyi entropy is a standard measure of the degree of coherence (i.e. pure state character) of a quantum state.[30] In retrospect, this is a very natural measure of Bose condensation, in which all particles go into the same pure state, which need not necessarily be an eigenstate of the system. Although quantum statistics have not been considered explicitly, it seems that the usefulness of the Renyi entropy as a measure of cooling will carry over completely into that regime.

The role of the radiation in heat pump cooling is to supply the power to drive the process and to synchronize the motion on the two surfaces of the two modes. The efficiency of the process with respect to power consumption is quite high, approximately 70%. The extra power is required to drive the system to its goal in finite time. This synchronization is crucial since the inverse unitary transformation is permissible which will cool the bath mode and heat the primary mode.

In the search for a unitary transformation the instantaneous approach was also employed. When the bath mode was cold (zero initial entropy) a solution was obtained able to heat the bath and cool the system. When both the system and the bath were hot with equal entropy only the optimal control procedure was able to find a solution leading to significant cooling.

The specific unitary transformation found by the optimal

control procedure is composed of an evaporative phase for about half the total time duration followed by a dump period where the excited surface population is transfered into the ground vibrational level of the primary mode.

The general cooling strategy adopted in this study is an active one. The strong fields applied are able to modify considerably the Hamiltonian of the system. This approach is therefore in the line of coherent control based on active intervention.[22] Existing schemes of laser cooling crucially depend on a passive component which is spontaneous emission. The slow rate of this process extremely limits the rate of cooling. The advantage of an active approach is twofold: The rates are controlled instead of waiting for spontaneous emission, and multilevel systems can be handled virtually just as easily as single level systems, which is essential for molecular cooling, where there is severe level congestion. However, the price payed for an active approach is that there is no built-in entropy sink it has to be provided within the larger system.

ACKNOWLEDGMENTS

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APPENDIX A: OPTIMAL CONTROL AND KROTOV'S METHOD

Optimal control theory (OCT) is a method for finding an optimal field which leads an initial state of the system to a target state in a finite time interval $\{0,t_f\}$. In quantum mechanics this objective is represented by a target operator $\hat{\mathbf{A}}$. OCT formulates this as a variation problem. The radiation field is the agent of control. An iterative procedure is used to find the solution. A maximum value of the objective

$$J=tr\{\hat{\mathbf{A}}\hat{\rho}(t_f)\} \tag{A1}$$

which is a functional of the control field $\epsilon(t)$ has to be found. Two constraints are imposed:

1. The evolution of the system is governed by Liouville-von Neumann equation.
2. Minimizing the total field energy.

These two constraints lead to the modified objective:

$$\overline{J}=tr\{\hat{\mathbf{A}}\hat{\rho}(t_f)\}-\int_0^{t_f}tr\left\{\left(\frac{\partial\hat{\rho}}{\partial t}-\mathscr{L}(\hat{\rho})\right)\hat{\mathbf{B}}\right\}dt - \lambda\int_0^{t_f}|\epsilon|^2dt, \tag{A2}$$

where $\hat{\mathbf{B}}$ is an operator Lagrange multiplier and λ is a scalar Lagrange multiplier. Integration by parts leads to

$$\overline{J}=tr\{\hat{\mathbf{A}}\hat{\rho}(t_f)\}-tr\{\hat{\rho}\hat{\mathbf{B}}\}|_0^{t_f}+\int_0^{t_f}tr\left\{\hat{\rho}\frac{\partial\hat{\mathbf{B}}}{\partial t}\right\}dt + \int_0^{t_f}tr\{\mathscr{L}(\hat{\rho})\hat{\mathbf{B}}\}dt-\lambda\int_0^{t_f}|\epsilon|^2dt. \tag{A3}$$

Two alternative solutions have been used. According to OCT an extremum for the objective J has to be found. This is done by variation of J with respect to $\delta\hat{\rho}$, $\delta\,\mathrm{Real}(\epsilon)$ and $\delta\,\mathrm{Imag}(\epsilon)$. The other approach, Krotov's method, is to maximize ΔJ. $\Delta J=J^{(k+1)}-J^{(k)}$, where $J^{(k)}$ is the objective in the k'th iteration. From Eq. (A3) ΔJ becomes:

$$\begin{aligned}\Delta\overline{J}=&tr\{\Delta\hat{\rho}\hat{\mathbf{A}}\}-tr\{\Delta\hat{\rho}\hat{\mathbf{B}}\}|_0^{t_f}+\int_0^{t_f}tr\left\{\Delta\hat{\rho}\frac{\partial\hat{\mathbf{B}}}{\partial t}\right\}dt\\&+\int_0^{t_f}tr\{\mathscr{L}^{(k)}(\Delta\hat{\rho})\hat{\mathbf{B}}\}dt+\int_0^{t_f}tr\{\Delta\mathscr{L}(\hat{\rho}^{(k+1)})\hat{\mathbf{B}}\}dt\\&-2\lambda\ \mathrm{Real}\int_0^{t_f}\epsilon^{(k)}\Delta\epsilon^{\star}dt-\lambda\int_0^{t_f}(\mathrm{Real}(\Delta\epsilon)^2\\&+\mathrm{Imag}(\Delta\epsilon)^2)dt.\end{aligned} \tag{A4}$$

The first four terms do not depend on $\Delta\epsilon$ explicitly. Therefore these terms do not contribute to ΔJ. This condition, with the condition that $\Delta\hat{\rho}(0)=0$, leads to the following equations:

$$\frac{\partial\hat{\rho}}{\partial t}=\mathscr{L}(\hat{\rho}), \tag{A5}$$

$$\frac{\partial\hat{\mathbf{B}}}{\partial t}=-\mathscr{L}^{+}(\hat{\mathbf{B}}), \tag{A6}$$

$$\hat{\mathbf{B}}(t_f)=\hat{\mathbf{A}}. \tag{A7}$$

Eq. (A5) is the condition that the density operator $\hat{\rho}$ will evolve in time according to the Liouville-von Neumann equation. Eq. (A6) is the equation of motion for the operator Lagrange multiplier $\hat{\mathbf{B}}$. Eq. (A7) is the final condition of Eq. (A6). These are the same equations obtained from OCT (Eqs. (2.11)–(2.13)). Three terms in Eq. (A4) depend on $\Delta\epsilon$:

$$\Delta\overline{J}=\Delta\overline{J(1)}+\Delta\overline{J(2)}+\Delta\overline{J(3)}, \tag{A8}$$

where

$$\Delta\overline{J(1)}=\int_0^{t_f}tr\{\Delta\mathscr{L}(\hat{\rho}^{(k+1)})\hat{\mathbf{B}}\}dt, \tag{A9}$$

$$\Delta\overline{J(2)}=-2\lambda\ \mathrm{Real}\int_0^{t_f}\epsilon^{(k)}\Delta\epsilon^{\star}dt, \tag{A10}$$

$$\Delta\overline{J(3)}=-\lambda\int_0^{t_f}(\mathrm{Real}(\Delta\epsilon)^2+\mathrm{Imag}(\Delta\epsilon)^2)dt. \tag{A11}$$

The integrand in $\Delta\overline{J(2)}$ is highly oscilatory and therefore $\Delta J(2)$ has negligible contribution to ΔJ. For the other two terms a maximum value for ΔJ is obtained by maximizing the integrands. The the problem of maximizing ΔJ has there-

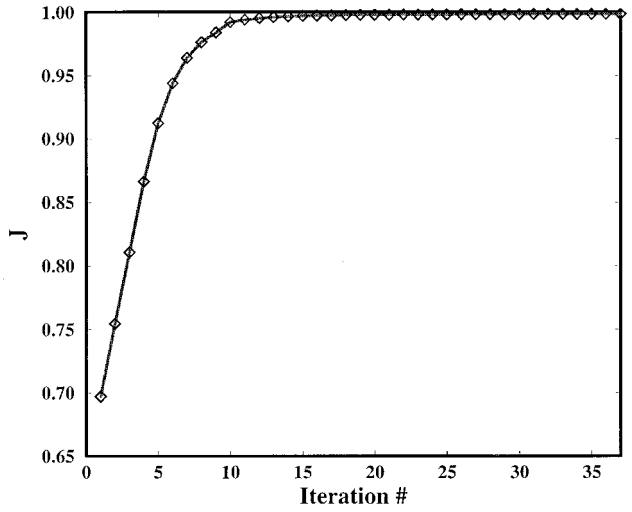

FIG. 19. The objective functional J as a function of the iteration number in the Krotov method.

fore been reduced to maximizing a quadratic equation in $\Delta\epsilon$. Taking the derivatives of Eqs. (A9) and (A11) with respect to Real($\Delta\epsilon$) and Imag($\Delta\epsilon$) and equating to zero lead to

$$tr\left\{\frac{\partial\Delta\mathscr{L}}{\partial\ \mathrm{Real}(\Delta\epsilon)}\hat{\rho}^{(k+1)}\hat{\mathbf{B}}^{(k)}\right\}-2\lambda\ \mathrm{Real}(\Delta\epsilon)=0, \quad \text{(A12)}$$

$$tr\left\{\frac{\partial\Delta\mathscr{L}}{\partial\ \mathrm{Imag}(\Delta\epsilon)}\hat{\rho}^{(k+1)}\hat{\mathbf{B}}^{(k)}\right\}-2\lambda\ \mathrm{Imag}(\Delta\epsilon)=0. \quad \text{(A13)}$$

The field for the $k+1$ iteration is obtained from Eq. (A12) and Eq. (A13)

$$\epsilon^{(k+1)}=\epsilon^{(k)}+\Delta\epsilon. \quad \text{(A14)}$$

With Eqs. (A12), (A13), (1.6) and (1.1), $\Delta\epsilon$ becomes

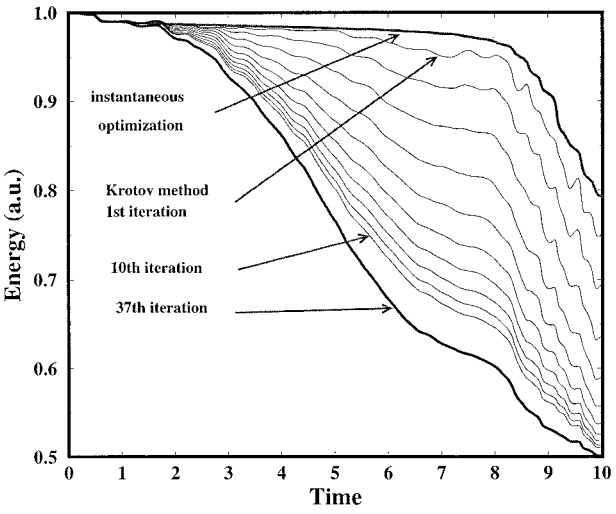

FIG. 20. The energy as a function of time for the instantaneous optimization approach the topmost graph, and the optimization cycles of the Krotov method.

$$\Delta\epsilon=\frac{-i}{\lambda}tr\{\hat{\rho}_c^{(k+1)}\hat{\mu}\hat{\mathbf{B}}_e^{(k)}+(\hat{\rho}_g^{(k+1)}\hat{\mu}-\hat{\mu}\hat{\rho}_e^{(k+1)})\hat{\mathbf{B}}_c^{(k)}-\hat{\mu}\hat{\rho}_c^{(k+1)}\hat{\mathbf{B}}_g^{(k)}\}. \quad \text{(A15)}$$

The algorithm for finding the best field is as follows:

(1) Propagate backward in time from time $t=t_f$ to time $t=0$ the target operator $\hat{\mathbf{A}}$ [Eq. (A7)] with the field from the k'th iteration $\epsilon^{(k)}(t)$.
(2) Apply Eqs. (A14), (A15) with $\hat{\rho}(0)$ and $\hat{\mathbf{B}}(0)$ to calculate $\epsilon^{(k+1)}(0)$.
(3) Use $\epsilon^{(k+1)}(0)$ to propagate $\hat{\rho}$ to time Δt.
(4) Calculate $\Delta\epsilon(\Delta t)$ by applying step 2 to $\hat{\rho}(\Delta t)$ and $\hat{\mathbf{B}}(\Delta t)$.
(5) Repeat step 3 and 4 until the final time $t=t_f$.
(6) Repeat steps 1 to 5 untill convergence is achieved.

Figure 19 shows the convergence of the Krotov method. It is clear that the iteration procedure saturates. The saturated value is used in the text as the optimal result of the Krotov method.

Figure 20 shows the convergence cycles of the Krotov method compared to the instantaneous optimization approach for the two mode model with the initial condition (3.3). The first iteration is from the instantaneous optimization and the Krotov method is able to improve significantly on this result.

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