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Laser cooling of molecules via single spontaneous emission

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Abstract. A general scheme for reducing the center-of-mass entropy is proposed. It is based on the repetition of a cycle, composed of three concepts: velocity selection, deceleration and irreversible accumulation. Well-known laser techniques are used to represent these concepts: Raman π-pulse for velocity selection, STIRAP for deceleration, and a single spontaneous emission for irreversible accumulation. No closed pumping cycle nor repeated spontaneous emissions are required, so the scheme is applicable to cool a molecular gas. The quantum dynamics are analytically modelled using the density matrix. It is shown that during the coherent processes the gas is translationally cooled. The internal states serve as an entropy sink, in addition to spontaneous emission. This scheme provides new possibilities to translationally laser-cool molecules for high precision molecular spectroscopy and interferometry.

PACS. 32.80.Pj Optical cooling of atoms; trapping – 33.80.Ps Optical cooling of molecules; trapping – 42.50.Vk Mechanical effects of light on atoms, molecules, electrons, and ions

1 Introduction

The existing laser cooling schemes [8] for atoms are based on the concept of a repeated cycle of optical pumping followed by spontaneous emission which transfers the atoms back into a resonant ground state. However, laser cooling of the translational motion of *molecules* is a formidable challenge due to the difficulty of maintaining such a closed optical pumping cycle. The reason is that due to the additional degrees of freedoms (vibration and rotation of the nuclei) optical spontaneous emission also populates non-resonant states and thus interrupts the cycle. Bahns *et al.* [1] have proposed a scheme that cures this problem using a multiple single-frequency laser. Vuletic and Chu [2] proposed to use losses in an optical cavity instead of spontaneous emission. So far, there has been no established laser cooling scheme for molecules. Currently, there are three main non-laser techniques which are able to produce moderately cold molecules. These techniques are photoassociation [3], buffer gas cooling [4] and phase space rotation with deceleration in Stark decelerator [5]

In this paper, we propose a cooling scheme for molecules which uses coherent laser techniques and a single spontaneous emission. Although we emphasize on molecules, the scheme also applies to atoms. The entropy of the translational molecular motion is coherently transferred to the internal degrees of freedom of the molecule, thus avoiding the problem associated with (repeated) spontaneous emission. Although it is well-established that a coherent process cannot change the *total* entropy of a quantum system, the entropy of a subsystem can be changed by unitary transformation which act on the total system. An example is the work of Scully [9] who devised a 'quantum maser engine' which extracts work in the form of maser radiation from a thermal heat bath. The reduction in the internal entropy is accompanied by the increase in the center of mass (c.m) entropy although there is no dissipation and the whole system entropy is unchanged. A single spontaneous emission is employed to each molecule to achieve irreversibility.

We shall refer to the internal energy levels, the c.m momentum and the atom/molecules system as the *internal* (subscript "I"), *external* (subscript "cm") *and total* (subscript "tot") subsystems (degrees of freedoms) respectively, which are coherently coupled together by lasers and coupled to the quantized *radiation* degree of freedom *via* spontaneous emission. In Section 2, we present a general idea of the cooling scheme. In Section 3, we use well-known laser techniques to construct a general laser cooling scheme which applies to molecular gas. In Section 4, we obtain analytical density matrix for the scheme and model the populations dynamics analytically. This enables convenient computation of the subsystems entropies in Section 5.

2 New cooling concept

In c.m cooling of a gas, the initially large momentum width of an ensemble is decreased. For pre-cooled molecules we propose a general cooling concept based on

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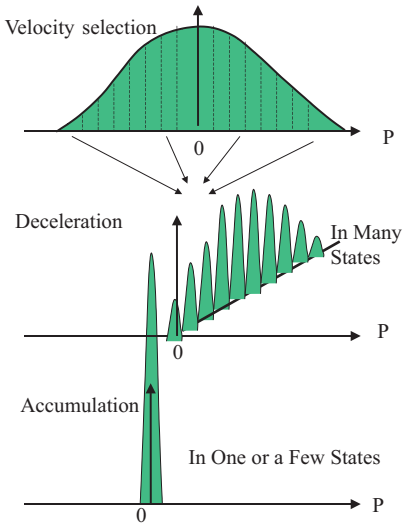

Fig. 1. General translational cooling scheme based on the concepts of velocity selection, deceleration and accumulation.

the repetition of a *cycle*, each composed of three sequential *steps*: (1) velocity selection, (2) deceleration and (3) accumulation. Assume that one can divide the ensemble into narrow slices of narrow momentum width, decelerate each slice to zero mean and accumulate all the narrow slices with zero mean. This process results in a cooling of the gas (Fig. 1). Alternatively, we can also select and accumulate a narrow population around *zero velocity* from the ensemble and decelerate the ensemble a little to fill back the (non-accumulated) population with zero velocity (another laser cooling scheme for molecules entitled "Laser Cooling of Molecules by Zero Velocity Selection", by C.H. Raymond Ooi, has been submitted).

In this paper, we wish to demonstrate that this new concept is generally applicable for translational cooling. We shall use well-known laser techniques to construct a laser cooling scheme, which we will analytically model using the density matrix. The scheme is unique as it applies to cooling of molecules where existing laser cooling techniques for atoms [8] fail. We focus on analyzing the entropies of subsystems in the process of cooling and leave out the specific details of molecular levels since they are not important to demonstrate the concept of the scheme.

3 Laser cooling scheme

For fast cooling, laser pulses are good options. The Raman π-pulse technique [10] is used for narrow velocity width selection, repeated alternating STIRAP processes [11] for deceleration and a single optical spontaneous emission for irreversible accumulation (Fig. 2). We start with a precooled molecular gas with a temperature T of less than 1 K, which are readily obtained from the magnetic trap [4] or electrostatic trap [5]. These molecules occupy essentially a single vibrational and rotational level in the ground electronic state, but may be in more than one magnetic quantum states. The molecules in a single internal initial state, referred as $|g0\rangle$ can be obtained either by spatial separation by state (Stern-Gerlach effect) using laser fields [6] or adiabatic population transfer [7]; or simply by laser pumping. Thus, the gas has zero internal entropy but finite c.m entropy.

These molecule are released from the trap. We use rapid laser pumping techniques to quickly cool the molecules with a large thermal c.m momentum width of $\sqrt{2Mk_{\rm B}T}$ before they expand beyond the laser interaction region. We consider a sufficiently dilute gas, with collisional lifetime shorter than the duration of each velocity selection and a STIRAP cycle. Thus, it is justified to ignore any collisional dynamics during these laser interaction processes. Once the molecules have been translationally cooled, it is possible to confine them in a shallow trap and compressed to higher density. Elastic collisions rethermalize the molecules and lead to three dimensional cooling. However, the gas density cannot be too high in order to minimize trap loss due to inelastic collisions.

3.1 Velocity selection

The velocity selection works within the internal states referred as $|e\rangle, |g0\rangle$ and $|g+\rangle$ while the deceleration are based on the states $|e\rangle, |g-\rangle$ and $|g+\rangle$ (Figs. 2a and 2b). During velocity selection (Fig. 2a) which takes typically 10 μs for a momentum width of 1 cm s $^{-1}$, a fraction of molecules with narrow momentum width and mean momentum P is selected from the population in state $|g0\rangle$ and transferred to an empty state $|g+\rangle$ using a π-pulse, without populating the excited state. This step is in principle the same as described in reference [10] except that here we use orthogonal $lin - \sigma^+$ lasers instead of 1-D counter propagating $\sigma^+ - \sigma^-$ lasers because we start from the state $|g0\rangle$ with $M = 0$. A narrow velocity width $\Delta v_{\rm vs}$ can be selected by using longer pulse duration.

3.2 Deceleration

The selected population is decelerated (Fig. 2b) using a sequence of STIRAP processes which has been shown experimentally to be highly efficient in molecules like SO_2 and Na_2 [14]. It has also been used for coherent momentum transfer in atom optics and atom interferometry [7]. In principle, a non-optical deceleration technique [12] could also be applied for this step; but it is slower. In the optical regime, STIRAP provides rapid deceleration of the velocity selected population towards zero mean momentum by repeated population inversion between the *Raman states* $|g+\rangle$ and $|g-\rangle$. In each inversion, defined as a *substep* of step 2, a pair of counter propagating, overlapping and counter-intuitive sequence $\sigma^+ - \sigma^-$ polarized pulses transfers $2\hbar k$ of photon momentum within about 0.1 μs, corresponding to a deceleration of $10^4 g$. By repeatedly reversing the directions and sequence of the pulses, we obtain a rectified force acting on the velocity-selected population which reduces its kinetic energy towards zero. Thus, we have decelerated a fraction ("slice") of the total number

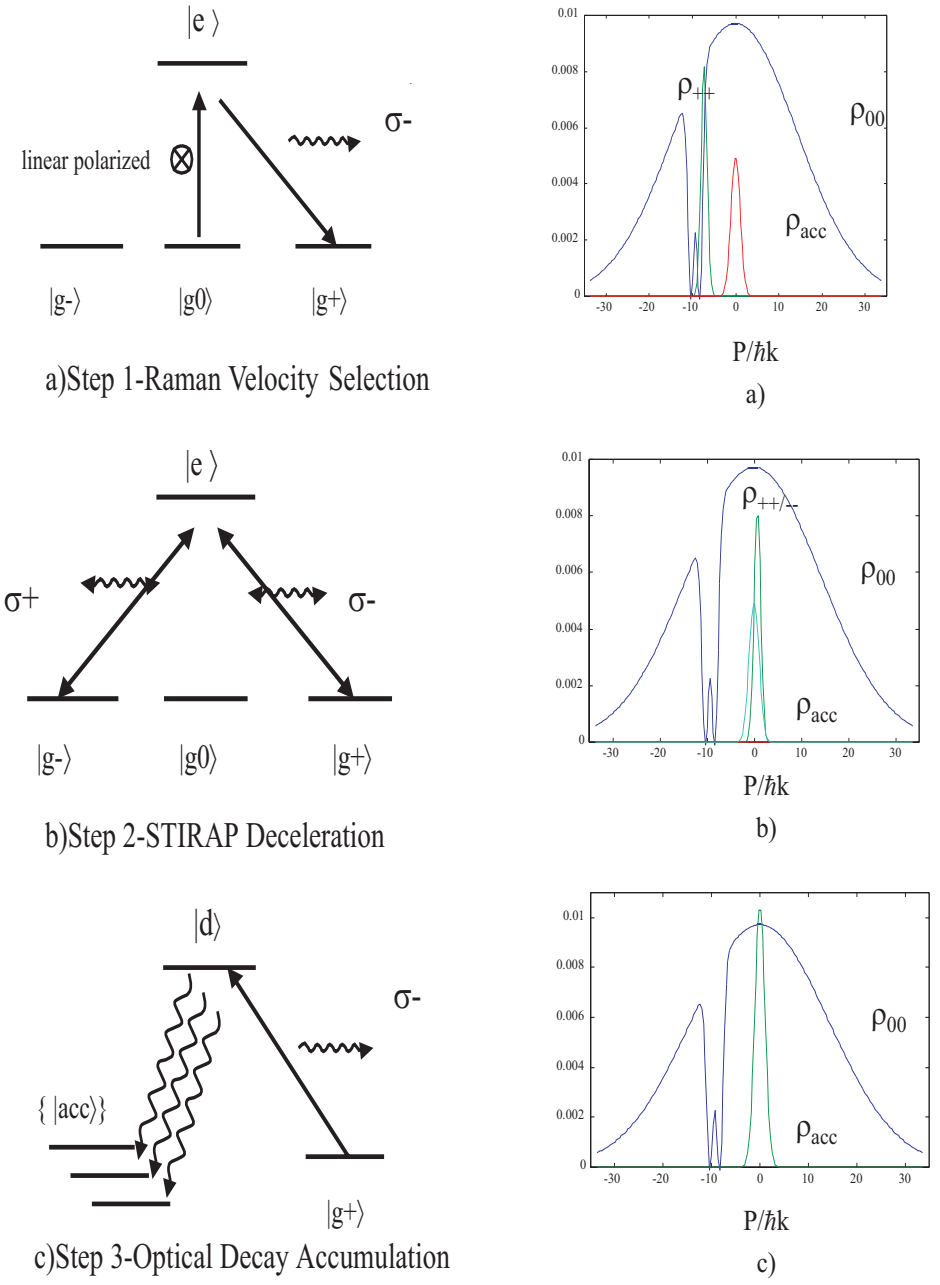

Fig. 2. Schematic diagrams for a laser cooling cycle composed of 3 sequential steps: (a) Raman velocity selection, (b) STIRAP deceleration of selected molecules and (c) accumulation by single optical spontaneous emission to one of the many accumulation states. On the right side are examples of the momentum distributions of the internal populations corresponding to each step.

of molecules. The number laser pulses required for deceleration can predicted as the ratio of the selected velocity to the velocity selected width, $v_{\rm vs}/\Delta v_{\rm vs}$ without performing any measurement on the system. Since, the STIRAP efficiency is not 100%, the cooling is efficient only for a pre-cooled gas which requires not too many number of repeated STIRAP cycles.

The c.m degree of freedom is the source of entropy. In the coherent processes of steps 1 and 2, the lasers provide a tool to remove kinetic energy and c.m entropy from the molecules through the entanglement of the internal and c.m degrees of freedom. The internal degree serves as the source of negentropy or entropy sink. We will show that the c.m entropy can be reduced during the coherent processes while the total entropy is constant.

3.3 Accumulation

We want to repeat steps 1 and 2 to accumulate the populations with narrow momentum slices and zero mean momentum. To avoid acceleration of those molecules that have been cooled by subsequent STIRAP processes, we introduce an irreversible process as the third step. Laser control processes are intrinsically reversible. However, it is possible to introduce "controlled irreversibility" by controlling the timing. For example, we can perform one way populations transfer to distinct internal states $|acc\rangle$ such as rovibrational states in molecules. When the laser field is switched off, reversibility has been broken. By doing so, we have irreversibly deposited each slice of narrow width population in different internal states, thus obtaining a

translationally cooled but internally hot ensemble. Here, translational cooling is achieved completely by coherent processes, at the expense of internal heating. However, this is difficult to achieve in practice as it requires many lasers with different frequencies and pulse duration or Rabi frequencies. Besides, the number of accumulation states $|acc\rangle$ has to be larger than the number of cooling cycles.

Here, we choose to rapidly transfer the populations from a Raman state ($|g+\rangle$ or $|g-\rangle$) to a decaying state $|d\rangle$, whereby subsequent spontaneous emissions populate the accumulation states $\{|acc\rangle\}$ (Fig. 2c). The decay rate and the number of accumulation states depend on the choice of $|d\rangle$. We take $|d\rangle$ to be the excited electronic state that decays with a short optical spontaneous emission lifetime 10^{-7} s to many rovibrational states. The final population of each of these accumulation states $|acc\rangle$ depends on the Franck-Condon factors of the molecules [15].

The whole cooling process involves the repetition of this cooling cycle by newly selecting a slice of molecules. We emphasize that each molecule undergoes only one cooling cycle with *a single spontaneous emission* to establish cooling. *No* repeated spontaneous emissions is required for cooling of each molecule. Therefore, closed pumping levels are not required. This makes the scheme applicable to cool molecules.

4 Analytical population dynamics

To describe the quantum dynamics of the density matrix associated with the molecular gas we use an analytical model for the dynamics of the populations during the interaction with the laser pulses. Initially, only one internal state $|g0\rangle$ is occupied and the c.m subsystem is in the thermal *Gibbs state* [17]. So, the initial total density operator is written as

$$\begin{aligned}\hat{\rho}_{\rm tot}(0) &= \hat{\rho}_{\rm I}(0)\otimes\hat{\rho}_{\rm cm}(0)\\ &= |g0\rangle\langle g0|\otimes\sum_P W(P)|P\rangle\langle P| \end{aligned} \quad (1)$$

where $W(P) = (1/Z)\mathrm{e}^{-P^2/\sigma^2}$ is the statistical weight, $Z = \sum_P \mathrm{e}^{-P^2/\sigma^2}$ is the partition function and $\sigma = \sqrt{2Mk_{\rm B}T}$ is the initial momentum width with temperature T [18].

The quantum dynamical evolution of the molecules in each cooling step and throughout the cooling process can be described analytically using the density matrix. This allows for convenient evaluation of the internal and c.m subsystems probability distributions and the corresponding entropies, which enables us to work out the cooling efficiency. With respect to the basis of internal eigenstates $\{|a\rangle\}$ and the c.m momentum states $\{|P\rangle\}$, the density matrices of the total system, internal subsystem and c.m subsystem are defined respectively as

$$\hat{\rho}_{\rm tot}(t) \doteq \sum_{a,b}\sum_{P,P'}\rho_{ab}(P,P',t)|a,P\rangle\langle b,P'| \quad (2)$$

$$\hat{\rho}_{\rm I}(t) \doteq {\rm Tr}_{\rm cm}\{\hat{\rho}_{\rm tot}(t)\} = \sum_{a,b}|a\rangle\langle b|\sum_P\rho_{ab}(P,P,t) \quad (3)$$

$$\hat{\rho}_{\rm cm}(t) \doteq {\rm Tr}_{\rm I}\{\hat{\rho}_{\rm tot}(t)\} = \sum_{P,P'}|P\rangle\langle P'|\sum_a\rho_{aa}(P,P',t) \quad (4)$$

where $\rho_{ab}(P,P',t) \doteq \langle a,P|\hat{\rho}_{\rm tot}(t)|b,P'\rangle$ are the total system density matrix elements, $a,b \in \{e,g0,g\pm,d,\{acc_j\}\}$ the internal states and $\{P,P'\}$ the c.m momenta along $\sigma\pm$ polarized lasers axis (defined as z-axis).

The time evolution dynamics of the total system in step 1 and step 2 are formally described by the 3-level Bloch equations [19]. In step 1 the total system states are $|g0,P\rangle, |e,P\rangle$ and $|g+,P-\hbar k\rangle$. A STIRAP inversion from $|g+\rangle$ to $|g-\rangle$ in step 2 involves the momentum family of states $|g+,P+\hbar k\rangle, |e,P\rangle$ and $|g-,P-\hbar k\rangle$. Due to the reversal of the pulses during subsequent inversion from $|g-\rangle$ to $|g+\rangle$, the family of states becomes $|g-,P-\hbar k\rangle, |e,P-2\hbar k\rangle$ and $|g+,P-3\hbar k\rangle$. With the high populations transfer efficiency of STIRAP, the c.m coherences in the populations, for example $\langle g+,P-\hbar k|\hat{\rho}_{tot}(t)|g+,P-3\hbar k\rangle$ are negligibly small after each STIRAP pulse has been completed. We start with populations in the internal state $|g0\rangle$ and the c.m Gibbs state with no coherences between momentum states. So, the only non vanishing matrix elements are $\rho_{00}(P,P,0)$. The processes of a velocity selection, a STIRAP inversion and a spontaneous emission do not create new c.m coherences. Therefore, the populations remain diagonal in momentum basis throughout the cooling process: $\rho_{aa}(P,P',t) = \rho_{aa}(P,P,t)\delta_{P,P'}$.

On the other hand, during the transitions between different internal states, the non vanishing matrix elements between different internal states $\rho_{a,b\neq a}$ must contain the c.m coherences $P \neq P'$ due to momentum recoil: $\rho_{ab}(P,P',t) \neq 0$ and $\rho_{ab}(P,P,t) = 0$. Accordingly, equations (3, 4) reduce to

$$\hat{\rho}_{\rm I}(t) = \sum_a C_a(t)|a\rangle\langle a| \quad (5)$$

$$\hat{\rho}_{\rm cm}(t) = \sum_P f(P,t)|P\rangle\langle P| \quad (6)$$

where the internal and c.m probability distributions are respectively defined as $C_a(t) \doteq {\rm Tr}_{\rm cm}\{\hat{\rho}(t)\} = \sum_P\rho_{aa}(P,P,t)$ and $f(P,t) \doteq {\rm Tr}_{\rm I}\{\hat{\rho}(t)\} = \sum_a\rho_{aa}(P,P,t)$. Thus, we only need to evaluate the diagonal density matrix elements $\rho_{aa}(P,P,t)$. This greatly facilitates the computation of the subsystem density matrices and the corresponding entropies. To simplify the mathematics, we can model the velocity selected momentum distribution by a Gaussian function of a narrow width $\sigma_{\rm vsel}(\ll\sigma)$. During step i ($i = 1,2,3$) of the Nth cooling cycle (subscript $N{:}i$), the time evolution of the populations in the states can be written analytically as the following.

4.1 Step 1 of Nth cycle

$$\rho_{00}(P,P,t_1)_{N:1} = W(P) - \sum_{j=1}^{N-1} V_j(P) - V_N(P)h_1(t_1) \tag{7}$$

$$\rho_{++}(P,P,t_1)_{N:1} = h_1(t_1)W(P_N)\mathrm{e}^{-(P+\alpha\hbar k_{N,+}-P_N)^2/\sigma_{\mathrm{vsel}}^2} \tag{8}$$

where $0 \le t_1 \le \tau_1$, $h_1(t_1) = \sin^2 \pi t/2\tau_1$ and τ_1 is the duration of the velocity selection pulses, $V_j(P) \doteq W(P_j)\mathrm{e}^{-(P-P_j)^2/\sigma_{\mathrm{vsel}}^2}$ is the velocity selected distribution with mean momentum P_j, momentum width σ_{vsel} and mean population $W(P_j) \doteq (1/Z)\mathrm{e}^{-P_j^2/\sigma^2}$, k_{N+} is the σ^+ laser wavevector of the Nth cooling cycle and $\alpha = \mathrm{sgn}(P_j)$ determines the direction of the σ^+ laser to provide decelerating momentum kick.

4.2 Step 2 of Nth cycle

There are many substeps $n(= 1, 2, ... n_{\max})$ within step 2. The number of deceleration cycles $n_{\max}$ required to reduce the mean momentum from P_N to zero can be predicted as $n_{\max} = P_N/2\hbar k - 1/2$. Only the populations in states $|g+\rangle$ and $|g-\rangle$ change, according to

$$\rho_{aa}(P,P,t_2)_{N:2(n)} = h_2(t_2)W(P_N) \times \mathrm{e}^{-(P+\alpha\hbar k_{N,+}+\alpha\Lambda_n-P_N)^2/\sigma_{\mathrm{vsel}}^2} \tag{9}$$

$$\rho_{bb}(P,P,t_2)_{N:2(n)} = (1-h_2(t_2))W(P_N) \times \mathrm{e}^{-(P+\alpha\hbar k_{N,+}+\alpha\Lambda_{n-1}-P_N)^2/\sigma_{\mathrm{vsel}}^2} \tag{10}$$

$$\rho_{++}(P,P,0)_{N:2(1)} = \rho_{++}(P,P,\tau_1)_{N:1} \tag{11}$$

where $a = -$, $b = +$ for odd n (inversion from $|g+\rangle$ to $|g-\rangle$) and $a = +$, $b = -$ for even n. The time interval for every substep is $0 \le t_2 \le \tau_2$, $h_2(t_2) = sin^2\pi t/2\tau_2$, τ_2 is the duration for one inversion and $\Lambda_n \doteq \sum_{j=1}^{n} \hbar(k_{j+} + k_{j-}) \approx 2n\hbar k$ is the total amount of momentum transfer provided by n pairs of STIRAP pulses.

4.3 Step 3 of Nth cycle

The narrow populations from the Raman states $|g\pm\rangle$ are transferred rapidly to the decaying state $|d\rangle$ with a short π-pulse, the process is essentially unitary due to negligible spontaneous emissions from $|d\rangle$. This enables the replacement $\rho_{dd}(P,P,0)_{N:3} \approx \rho_{aa}(P,P,\tau_2)_{N:2(n_{\max})}$ as initial population and set $\rho_{\pm\pm}(P,P,t_3)_{N:3} = 0$. The population in $|d\rangle$ decays to many internal levels. Assuming that only a small branching ratio of the population from $|d\rangle$ decays back to $|g\pm\rangle$, the time evolution of the populations in step 3 is simply due to the spontaneous decays from $|d\rangle$ to M number of accumulation states $\{|acc_j\rangle, j = 1...M\}$ with the corresponding decay rates Γ_j. This is given by

$$\rho_{dd}(P,P,t_3)_{N:3} = \sum_{j=1}^{M} F_j \mathrm{e}^{-\Gamma_j t_3} W(P_N)\mathrm{e}^{-P^2/\sigma_{\mathrm{vsel}}^2} \tag{12}$$

$$\rho_{acc_j}(P,P,t_3)_{N:3} = F_j \frac{\sigma_{\mathrm{vsel}}}{\sigma_{acc}}\mathrm{e}^{-P^2/\sigma_{acc}^2} \times \left\{ \sum_{j=1}^{N-1} W(P_j) + W(P_N)(1-\mathrm{e}^{-\Gamma_j t_3}) \right\} \tag{13}$$

where $0 \le t_3 \le \tau_3$ is the time interval for step 3, τ_3 is the duration for $|d\rangle$ to empty its populations to essentially zero (taken as $10/\Gamma_j$) and F_j is the Franck-Condon factor for level $|acc_j\rangle$ with $\sum_{j=1}^{M} F_j = 1$. The accumulated momentum width σ_{acc} is slightly larger than σ_{vsel} due to the small momentum spread (about $0.5\hbar k_a$) from a single spontaneous emission. The normalization factor $\sigma_{\mathrm{vsel}}/\sigma_{acc}$ in equation 13 ensures that $\mathrm{Tr}_{\mathrm{tot}}\{\hat{\rho}_{\mathrm{tot}}\} = 1$ and can be estimated as $\sigma_{acc}/\sigma_{\mathrm{vsel}} \approx 1 + 0.5\hbar k_a/\sigma_{\mathrm{vsel}}$ where $k_a = (E_d - E_{acc})/\hbar c$.

The *total* density matrix in this step is diagonal in the basis states $|g0\rangle$, $|d\rangle$ and $\{|acc_j\rangle\}$ since these states are not coupled by lasers. The evolution is characterized by free spontaneous emission from $|d\rangle$ to $\{|acc_j\rangle\}$. Thus, the time evolution of the total density matrix for step 3 can be written as

$$\hat{\rho}_{\mathrm{tot}}(t_3)_{N:3} = \sum_P \{\rho_{00}(P,P,\tau_1)_{N:1}|0,P\rangle\langle 0,P| + \sum_{a=d,\{acc_j\}} \rho_{aa}(P,P,t_3)_{N:3}|a,P\rangle\langle a,P|\}. \tag{14}$$

5 Entropies

We proceed to evaluate the quantum (von Neumann) entropies [16]. The expressions for internal and c.m entropies are obtained from equations (5, 6) for discrete momentum [18] using $S_X(t) = \mathrm{Tr}_X\{\hat{\rho}_X(t)\ln\hat{\rho}_X\}$ where $X \in \{\mathrm{I}, \mathrm{cm}\}$

$$S_{\mathrm{I}} = -k_{\mathrm{B}} \sum_a C_a \ln C_a \tag{15}$$

$$S_{\mathrm{cm}} = -k_{\mathrm{B}} \sum_P f(P) \ln f(P). \tag{16}$$

From equation (1), the initial internal, c.m and total entropies are:

$$S_{\mathrm{I}}(0) = 0 \tag{17}$$

$$S_{\mathrm{cm}}(0) = -k_{\mathrm{B}} \sum_P W(P) \ln W(P) \tag{18}$$

$$S_{\mathrm{tot}}(0) = S_{\mathrm{cm}}(0). \tag{19}$$

Equations (15, 16) are valid for all times in all steps and take a simple form because the reduced density matrices are diagonal (Eqs. (5, 6)). Throughout the coherent interactions of step 1 and step 2 in the Nth cooling cycle, the total entropy takes a constant value of $S_{\rm tot}(\tau_3)_{(N-1):3}$. The total entropy changes only during incoherent process in step 3. Its time evolution in the Nth cooling cycle is given by

$$S_{\rm tot}(t_3)_{N:3} = -k_{\rm B}\sum_{P}\{\rho_{00}(P,P,\tau_1)_{N:1}\ln\rho_{00}(P,P,\tau_1)_{N:1} + \sum_{a=d,\{acc_j\}}\rho_{aa}(P,P,t_3)_{N:3}\ln\rho_{aa}(P,P,t_3)_{N:3}\}. \quad (20)$$

Each cooling cycle is completed in step 3, during which radiation entropy is created due to the random direction and many frequencies of the spontaneously emitted photons as the cooled molecules decay to the many $|acc\rangle$ states. We note that the existence of many $|acc\rangle$ states during step 3 leads to larger radiation entropy due to the frequency dispersion of the spontaneously emitted photons, in addition to the angular dispersion.

6 Results and discussions

In this section we will discuss in detail the result of our calculations and the evolution of the total system as well as the sub-systems corresponding to the c.m and the internal degrees of freedom. In each cooling cycle a fraction of molecules with a narrow momentum width is depleted from the state $|g0\rangle$ by velocity selection (Fig. 2a), slowed towards zero mean momentum *via* repeated inversion by STIRAP (Fig. 2b) and deposited irreversibly into the accumulation states (Fig. 2c).

The overall cooling effect is shown by the narrowing of the momentum probability distribution $f(P)$, which evolves from a large momentum width (about $30\hbar k$) to a narrow momentum width (about $2\hbar k$) with zero mean momentum (Fig. 5). The main interest of this paper is the c.m entropy $S_{\rm cm}$ which is found to decrease after the complete cooling process (Fig. 4a), in particular during velocity selection and deceleration since these steps move a fraction of the populations closer to zero momentum. This is the sign of *translational cooling by coherent processes* of steps 1 and 2 which contribute substantially to the reduction of $S_{\rm cm}$, from the maximum entropy of Gibbs state to the final populations with narrow momentum width. Throughout the cooling, the internal entropy $S_{\rm I}$ increases (Fig. 4a) due to the increase in the number of populated internal states. Within each cooling cycle, the laser fields have created correlations between internal and c.m momentum states. The internal states mediate the coupling between laser photons and the c.m momentum.

We proceed to elaborate on the detailed features of the entropy variations in each cooling cycle with regard to the populations of the internal and c.m states. During velocity selection, the transfer of a narrow momentum slice of population from a wide momentum distribution in $|g0\rangle$ is accompanied by one $\hbar k$ of momentum kick towards the center of the distribution. This leads to the reduction of $S_{\rm cm}$ (Fig. 3a). At the same time, the internal entropy $S_{\rm I}$ increases (Fig. 3b) because an additional internal state $|g+\rangle$ is populated.

In the deceleration step, $S_{\rm cm}$ is reduced in each substep (Fig. 3a) by repeated momentum kicks which push the selected populations closer to zero mean momentum. Entanglement [20] of the c.m momentum states during

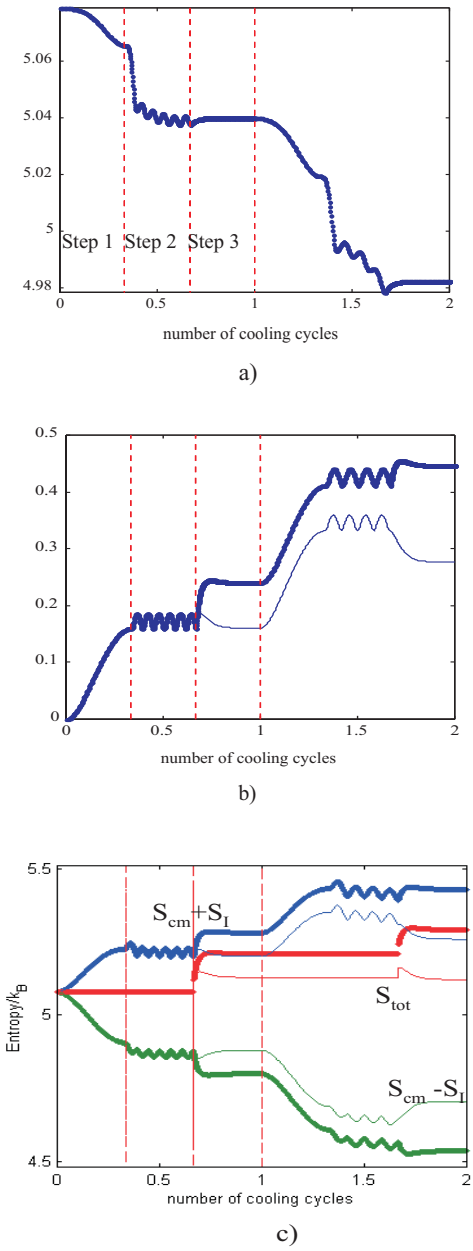

Fig. 3. Evolution of the (a) center of mass entropy $S_{\rm cm}$, (b) internal entropy $S_{\rm I}$, and (c) total entropy $S_{\rm tot}$ as well as $S_{\rm cm} \pm S_{\rm I}$ throughout the first 2 cooling cycles with 1 accumulation state (line with dots) and 10 accumulation states (solid line). The abscissa of each cooling cycle is equally divided for the 3 cooling steps, each with different timescale.

the STIRAP process increases the population dispersion of the c.m states. This explains the transient increase in $S_{\rm cm}$, which is less than the overall reduction of $S_{\rm cm}$ in one STIRAP process. During the first STIRAP process in step 2, this transient increase is not observed because it is quenched by the rapid reduction of $S_{\rm cm}$. The first STIRAP process reduces $S_{\rm cm}$ more than the subsequent ones. This quantitative difference is due to the nonlinear dependence of the entropy on the momentum distribution. However, $S_{\rm I}$ oscillates above a constant value (Fig. 3b). Each oscillation corresponds to a substep, which is an inversion by a STIRAP process. It can be explained by the creation of adiabatic states [21] resulting in the entanglement between states $|g+\rangle$ and $|g-\rangle$. This involves the population of an additional internal state, thereby increasing $S_{\rm I}$. After the completion of a STIRAP process, $S_{\rm I}$ falls back to the value before the entanglement.

The total entropy $S_{\rm tot}$ is of course constant throughout steps 1 and 2 but changes only during step 3. Figure 3c shows an important point in statistical physics, that the unitary evolution can effectively reduce the c.m entropy while the total entropy remains constant. It clearly indicates that *unitary or coherent process* alone is able to *substantially change the subsystem entropy or cool the subsystem*, in this case cooling of the c.m subsystem degree of freedom. This observation follows from the Araki-Lieb theorem for quantum entropy [22], $S(t) \leq S_{\rm I}(t) + S_{\rm cm}(t)$. For initial state where the subsystems are uncorrelated, $S(0) = S_{\rm I}(0) + S_{\rm cm}(0)$. After unitary process, the c.m degree is cooled if $S_{\rm I}(t) - S_{\rm I}(0) \geq S_{\rm cm}(0) - S_{\rm cm}(t) > 0$. Thus, in principle it is possible to establish coherent cooling of a subsystem by transferring its entropy to another subsystem(s). However, the cooling cannot be repeated for other molecules unless an irreversible process is introduced as part of the cooling cycle.

In step 3, a slight increase in $S_{\rm cm}$ arises due to momentum spread from the single spontaneous emission, but this is smaller than the decrease in $S_{\rm cm}$ in steps 1 and 2 (Fig. 3a). This leads to the overall reduction of $S_{\rm cm}$ in each cooling cycle. In fact, $S_{\rm cm}$ reduces substantially during the coherent processes (steps 1 and 2) instead of the spontaneous emission. The important role of the *single spontaneous emission* is to irreversibly accumulate the translationally cooled populations.

The entropy variations for a *single* $|acc\rangle$ state and *multi* $|acc\rangle$ states are shown in Figures 3b and 3c (we model 10 $|acc\rangle$ states with logarithmic Franck-Condon factors, $F_j = C \ln j$ with $\sum F_j = 1$ and a fixed decay rate). For a single $|acc\rangle$ state, $S_{\rm I}$ reduces during step 3 of the second cooling cycle because the number of internally populated states reduces from three populated states $(|g0\rangle, |g\pm\rangle, |acc\rangle)$ to two states $(|g0\rangle, |acc\rangle)$ (Fig. 3b). The c.m entropy $S_{\rm cm}$ is unaffected by the number of $|acc\rangle$ states (Fig. 3a). However, the internal entropy $S_{\rm I}$ increases with the number of $|acc\rangle$ states since the number of populated internal states increases (Fig. 3b). It is interesting to observe that the increase in $S_{\rm I}$ from populating 10 internal states (in step 3) is still smaller than the increase in $S_{\rm I}$ from velocity selection (step 1). This is because entropy is not simply a measure of the number of occupied states, but also depends on the relative populations among the states.

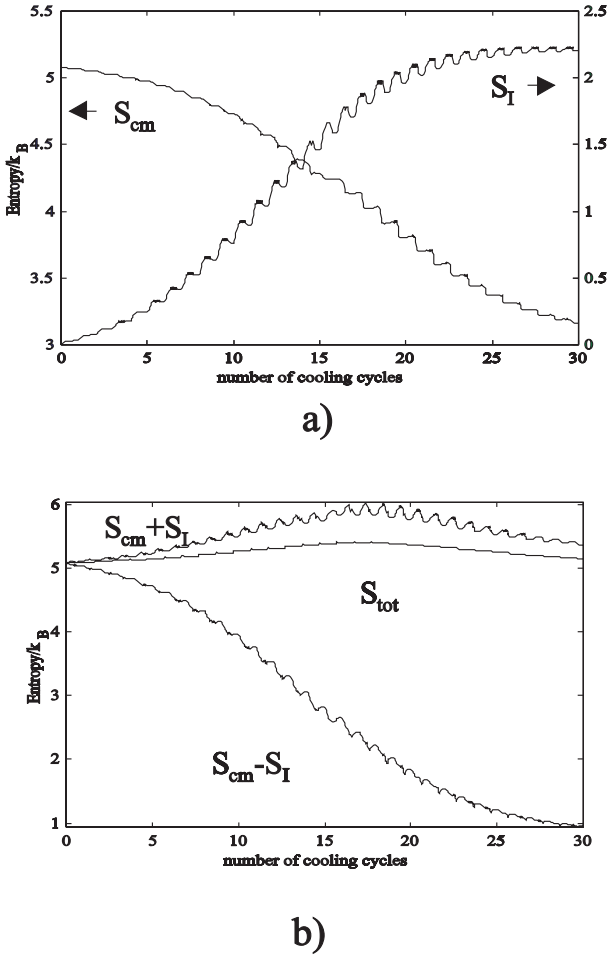

Fig. 4. Results after the whole cooling process with 10 accumulation states for (a) $S_{\rm cm}$ and $S_{\rm I}$, (b) $S_{\rm tot}$ and $S_{\rm cm} \pm S_{\rm I}$.

The internal and c.m entropies fluctuate throughout the cooling process (Fig. 4a). As the momentum width of the populations shrinks towards a narrow velocity selected width in the cooling process, the translational entropy $S_{\rm cm}$ reduces from a maximum towards zero. The small residual populations in the right and left wings of the narrow peak (Fig. 5) is due to inefficient velocity selection with Gaussian momentum profile. In practice, a more efficient pulse shape can be tailored to selectively transfer the narrow populations as close to a square momentum profile as possible. This would bring the final $S_{\rm cm}$ closer to zero in the end of the cooling process. On overall, $S_{\rm I}$ increases from zero, from population in one internal state to populations in multi internal $|acc\rangle$ states.

The total entropy $S_{\rm tot}$ does not decrease after the cooling (Fig. 4b). It seems that scheme with single spontaneous emission is unable to cool the total system. This is not true because the large number of internal $|acc\rangle$ states has contributed significantly to $S_{\rm tot}$. In our analysis with one $|acc\rangle$ state (this would apply to atoms with a closed

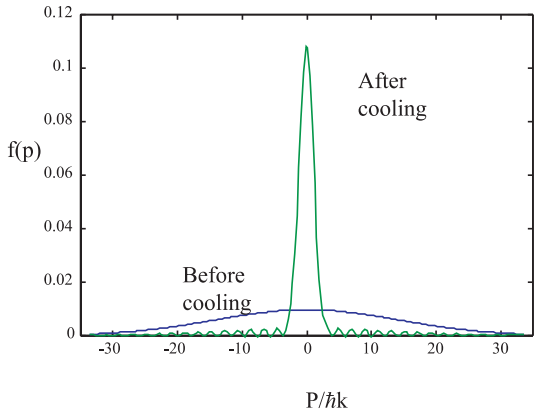

Fig. 5. Total momentum probability distribution $f(P)$ before and after the cooling process.

pumping cycle), we find significant decrease in $S_{\rm tot}$ as well as $S_{\rm cm}$. The cooling results are consistent with the general properties of quantum entropy as they satisfy the Araki-Lieb inequality [22], $|S_{\rm I} - S_{\rm cm}| \leq S_{\rm tot} \leq S_{\rm I} + S_{\rm cm}$, as shown in Figures 3c and 4b. The non-negligible index of correlation $I_{\rm C} = (S_{\rm cm} + S_{\rm I}) - S_{\rm tot}$ [17] shows that the internal and c.m subsystems are correlated by the laser interactions throughout the cooling process.

We note that the increase in the internal entropy is due to the specific choice of the accumulation scheme (step 3). The choice is determined by practical requirements. We choose $|d\rangle$ to be an excited electronic state so that the fast optical spontaneous emission decreases the total cooling time. This is at the expense of introducing many rovibrational $|acc\rangle$ states. The amount of increase in the internal and radiation entropies depend essentially on the number of $|acc\rangle$ states. The resulting internal heating is analogous to creation of radiation entropy. The many internal states in molecules provide an additional entropy sink, much like the radiational Fock states. During the cooling process, the translational entropy is removed irreversibly by spontaneous emissions to these entropy sinks.

The laser cooling model presented above does not consider the possibility of further infrared spontaneous decays from the $|acc\rangle$ states to lower rovibrational states for *heteronuclear diatomic* molecules. Within typically about 0.1 s, the molecules essentially end up in the ground vibrational state. Thus, the vibrational heating occurring in the model is a *transient* effect. The infrared spontaneous decay will lead to a vibrational cooling but also to a rotational heating of the molecule.

The applicability of the scheme is essentially limited to pre-cooled molecules since it requires the large number, s of STIRAP processes to decelerate the molecules. Since each STIRAP has an efficiency of less than 100 percent the number of non-cooled molecules grows with s. In a real experiment s should be less than 100. Since the maximal momentum transfer to the molecules is $\Delta p_{\rm M} = 2\hbar k s$ one can estimate that the initial thermal energy $\Delta p_{\rm M}^2/(2M)$ should not be larger than about 100 mK.

Our proposal only concerns with cooling in one spatial dimension. Although the molecules are translationally cold in a single momentum direction, they would be very useful for molecular spectroscopy and interferometry. For cooling in three dimensions an even larger number of STIRAP pulses is required. However, by setting up a trap which compresses the molecules after the cooling process, collisional thermalization may subsequently lead to a moderate 3-D cooling.

7 Conclusions

We have presented a scheme which decreases the c.m entropy of a gas through the coupling between the c.m, internal and radiation degrees of freedom. The scheme is based on the repetition of a cycle, composed of three concepts: velocity selection, deceleration and irreversible accumulation. We have modelled these concepts using the Raman velocity selection, STIRAP deceleration and a single spontaneous emission. It does not require a closed pumping cycle nor repeated spontaneous emissions. Therefore, the scheme is applicable to cool molecules. We have modelled the dynamics of the populations and studied the changes in the entropies. Simulations of the model show the reduction of the momentum width and the c.m entropy and thus demonstrate the cooling efficiency. The many internal states in molecules can serve as a useful entropy sink for translational cooling, in addition to the radiation entropy. This scheme should open up new possibilities for translational laser cooling of molecules, molecular spectroscopy and molecular interferometry.

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