We propose a laser cooling concept for translational motion of neutral molecules. The cooling works by repetition of a cooling cycle composed of three sequential steps: velocity selection of a narrow momentum width, deceleration of velocity selected molecules and irreversible accumulation. Those molecules which have been cooled undergo only one optical spontaneous emission for irreversible accumulation. This circumvents the problem of broken closed pumping cycle required for laser cooling by optical spontaneous emissions. We consider thermalized molecules at temperature of 1K as precursor and describe a rotational pumping scheme to prepare the molecules in an appropriate initial states for translational cooling. Using realistic cooling parameters, we estimate the cooling time and show that efficient cooling to a momentum width of $\sim \hbar k$ can be achieved within a practical timescale. The physical feasibility of the cooling concept is showned by developing a cooling model. This enables analytical description of the transient populations and entropies. Simulation shows that after the cooling process, a large momentum width is reduced to a narrow final width, determined by velocity selection. Translational cooling occurs through the reduction of the center of mass entropy, mainly during coherent laser interactions. The cooling process removes the translational entropy irreversibly to the radiation and internal entropy sinks.

I. INTRODUCTION

The existing laser cooling schemes for atoms have been successfully based on the concept of repeated optical excitation followed by spontaneous emission [1]. In molecules, there are additional motional degree of freedoms, namely the vibrational and rotational motions in addition to the center of mass translational motion. This creates two characteristics in molecules which are absent in atoms. First, the optical spontaneous emission (fluorescence) will inevitably repopulate more than one state. This makes existing cooling schemes for atoms unapplicable to molecules. Second, the existence of additional quantum states associated with the vibrational and rotational motions provide additional entropy sinks other than the radiation reservoir for translational cooling.

A scheme for sequential translational-vibrational-rotational cooling [2] has been proposed but not demonstrated yet. Existing schemes for sole vibrational cooling [3] use optimally controlled ultrashort pulses. A translational cooling scheme which uses cavity for incoherent processes of dissipation has been proposed [4]. Laser cooling of translational motion of molecules is more challenging due to the requirement of large momentum kick from optical photons to slow a molecule and the difficulty of maintaining an efficient closed optical pumping cycle, since fluorescence from the excited electronic state will populate other molecular levels and leads to inefficient returning to the original ground state. Closed cycles in far-infrared and microwave regimes are available but may not be favorable due to their low spontaneous emission rates. Thus, a closed optical pumping cycle which involves repeated optical spontaneous emissions cannot be simply established in molecules for continuous removal of the translational kinetic energy and entropy.

In this work, we circumvent the problem by first establishing efficient closed optical pumping cycles based on coherent processes of Raman velocity selection and STIRAP (Stimulated Raman Adiabatic Passage) [6] to continuously reduce the translational kinetic energy of a narrow velocity class of molecules to near zero. Then, this cooled class of molecules is pumped to irreversibly populate other rovibrational states through a single optical spontaneous emission. These molecules need no further recycling and are decoupled from lasers. This is the main ingredient for successful translational cooling of molecules. Our cooling scheme do not introduce permanent vibrational heating, since the
molecules subsequently undergo infrared decay mainly to the low vibrational levels in about 1s. As in existing vibrational cooling schemes [3], the decay inevitably leads to some rotational heating. If necessary, this would need a separately rotational cooling scheme, which will be reported in our future work. Our aim here is for translationally cooled molecules, which would be invaluable assets for molecular physics since they can be confined in shallower and more handy traps for convenient manipulations, fundamental studies and further internal coolings.

In Section II, we elaborate our cooling concept in a general way. Then, in Section III we describe how the molecules to be translationally cooled, can be appropriately prepared in practice using a rotational pumping scheme and buffer gas cooled molecules [7]. The cooling scheme is shown to be feasible in two aspects; in practice (as shown in Section IV by estimates of physical quantities) and in principle (as shown in Section V by modelling of the cooling process). We show that the velocity selection, normally used for subrecoil cooling [5] [8] can be practically used to cool molecules from 1κ to Doppler temperature. We model the cooling process with analytical density matrix and study the entropy change of the system. The translational entropy is found to reduce mostly during the coherent deceleration and velocity selection steps. Although an irreversible process from the single spontaneous emission per molecule is necessary for cooling and leads to the increase in the radiation entropy, it does not contribute substantially to the translational entropy reduction.

II. COOLING CONCEPT

In this paper, we propose a laser cooling concept for the translational motion of neutral molecules. We describe the cooling process with an analytical model and demonstrate the cooling results by numerical simulations. The cooling process is based on the repetition of a cooling cycle, each composed of three different physical steps: 1) velocity selection, 2) deceleration and 3) accumulation. We refer to the molecules as a total system (subscript ‘tot’) with two subsystems: the electronic, vibrational and rotational states as the internal degree of freedom (subscript ‘I’) and the molecular center of mass as the external degree of freedom (subscript ‘cm’). The velocity selection and deceleration involve 4 internal levels, 3 ground states |g0, ±⟩ corresponding to the states with magnetic quantum number M = 0, ±1 and an excited state |e⟩ (M = 0) (Fig. 2a and 2b). The states |e⟩, |g0⟩ and |g+⟩ are used for velocity selection while the deceleration are based on the states |e⟩, |g−⟩ and |g+⟩. For convenience, we may refer to |g0⟩ and |g±⟩ as initial state and Raman states respectively.

The translational cooling starts with the first step, which is the velocity selection. (see Fig. 2a and 3a). A fraction of molecules with narrow momentum width and mean momentum $P$ is selected from the population in state |g0⟩ and transferred to an empty state |g+⟩ using a $\pi$-pulse, without populating the excited state. This step is essentially the same as described in Ref. [8] except that here we use orthogonal $\sin - \sigma^+$ lasers instead of counter propagating $\sigma^+$ - $\sigma^-$ lasers, since the dipole moment between states |g0⟩ and |e⟩ is aligned along the $\sigma^+$ polarized laser axis.

In the second step (see Fig. 2b and 3b), the selected molecules are decelerated using a coherent process. In principle, non-optical deceleration technique can be applied [10]. However, for practical reasons, we require efficient and fast optical momentum transfer by repeated population inversion between the Raman states |g+⟩ and |g−⟩. This can be accomplished by various population transfer techniques using optimally engineered laser pulses [11]. Here, we adopt the STIRAP process which has been shown to be highly efficient in molecules [6] [12] and has been used for coherent momentum transfer in atom optics and atom interferometry [13]. In this step, the internal populations are repeatedly inverted between |g+⟩ and |g−⟩. Each inversion is a substep of step 2, which is accomplished by reversing the directions and the counter-intuitive sequence of a pair of counter propagating $\sigma^+$ and $\sigma^-$ polarized pulses. Each pair of the STIRAP pulse provides about $2\hbar k$ of photon momentum kick to decelerate the molecules. Thus, the population with a mean momentum $P$ will require a number of $P/2\hbar k$ STIRAP inversions to reduce the mean momentum $P$ towards zero. In the end of this step, we have a fraction of molecules with the translational energy close to zero.

We want to repeat steps 1 and 2 to accumulate the populations with narrow momentum width around zero momentum. Since steps 1 and 2 are coherent processes, subsequent repetition of these steps would not lead to net cooling because the next STIRAP process would accelerate the molecules out of zero mean momentum. The Raman states must be emptied before the next deceleration cycle starts. We achieve this with an irreversible process in the third step (see Fig. 2c and 3c). The cooled and decelerated molecules are rapidly transferred from the Raman states to a decaying state |d⟩ which may be an excited electronic state or a rovibrational state in the ground electronic state. Due to the requirement of fast translational cooling of unconfined molecules, we use an excited electronic state which provides fast optical spontaneous decay time. Subsequent spontaneous emissions populate the many vibronic ground as the accumulation states {acc}. We emphasize that there is no vibrational heating as time passes, since the molecules in states {acc} are decoupled from the laser beams and will undergo tens of infrared spontaneous decays to the lowest vibrational levels in about 1s. This introduces additional momentum spread in the order of an
optical photon momentum, much smaller than the overall reduction of momentum width. It is the irreversibility of the spontaneous emission which enables repeated accumulation of the molecules with narrow momentum slices and zero mean momentum from each cooling cycle as steps 1, 2 and 3 are repeated.

Each cooling cycle which is composed of a sequence of the three steps described above, begins with the velocity selection of a new slice of narrow momentum width. The whole cooling process involves the repetition of the cooling cycle. We point out that the equivalent temperature of the molecules after the process corresponds to the velocity selected momentum width, which can be well below the recoil limit.

The main difficulty to laser cool molecules by repeated spontaneous emissions in the optical regime is due to the fluorescence decay from an excited electronic state to many rotational-vibrational states of the ground electronic state. After a spontaneous emission, the molecules have a high probability of not returning to the original state. Thus, the molecules decay to a state which is off-resonant with the pumping laser before their momenta are reduced by the laser photons. In our cooling scheme, the momentum and kinetic energy of each molecule are quickly reduced toward zero by deceleration (step 2) before undergoing a single optical spontaneous emission process in the end of a cooling cycle. Thus, each cooling cycle completely cools a particular fraction of molecules. This cooling scheme circumvents the requirement of repeated spontaneous emissions for each molecule to obtain cooling. It is this unique feature which makes translational laser cooling of molecules possible.

III. PREPARATION OF INITIAL MOLECULES

Initially, the molecules to be translationally cooled can be prepared in a thermal equilibrium of 1K by the versatile buffer gas cooling [7], with a single heavily populated internal state |g0⟩ and two empty states |g±⟩ using a rotational pumping scheme described below.

A. Thermalized molecules

We start with the preparation of thermalized molecules which can have sufficiently few internal states for convenient rotational pumping and sufficiently low translational temperature for practical translational cooling in unconfined space. We emphasize that we are dealing with neutral molecules instead of molecular ions. Neutral molecules produced by laser ablation are highly excited internally and translationally. Buffer gas cooling is a good technique to thermalize the molecules, reduce the translational temperature of 1K and depopulate many of the highly excited vibronic and rotational states. Elastic collisions during buffer gas cooling provides a good thermalization mechanism to bring the molecules close to thermal equilibrium. At thermal equilibrium of temperature \( T_i \), the populations of the ground electronic surface \(|\Sigma\rangle\) are distributed among rovibrational states \((n, J)\) according to the Maxwell-Boltzmann distribution [14]

\[
P(n, J) \propto (2J + 1) \exp\left(-\frac{\hbar c BJ(J + 1) - \hbar c v(n + \frac{1}{2})}{k_B T_i}\right)
\]  

(1)

where \( v \) and \( B \) are vibrational and rotational constants (in wavenumber) respectively. The maximum population corresponds to \( n_{\text{max}} = 0, J_{\text{max}} \approx \sqrt{\frac{k_B T_i}{2 \hbar^2 c B}} - \frac{1}{2} \). At initial temperature of \( T_i = 1K \) and \( B \approx 0.1 cm^{-1} \), the molecules are mainly in the ground electronic state with the highest populations in \( n = 0 \) and \( J_{\text{max}} \approx 1 \) or 2. Thus, the molecules are reasonably cold internally and this makes it easy to create a single heavily populated state |g0⟩ for subsequent translational cooling. Since the excited vibrational states are scarcely populated, molecular collisions rates are small and can be neglected [15].

B. Rotational Pumping

We wish to create 2 empty states |g±⟩ and a heavily populated state |g0⟩ for more efficient translational cooling. This can be done by pumping the populations from the most highly populated rotational sublevels into a single sublevel within the ground vibrational and ground electronic state, namely \(|g0\rangle = |\Sigma, n = 0, J = 1, M_J = 0\rangle\) (see Fig. 1). Using \( \sigma^+ \) polarized laser, the populations in rovibrational states \(|n, J, M_J\rangle = |0, 1, -1\rangle, |0, 2, -2, -1, 0\rangle\) are excited to states \(|1, 0\rangle, |1, 1, -1, 0, 1\rangle\) respectively. On the other hand, \( \sigma^- \) polarized laser (same frequency as \( \sigma^+ \))
excites the populations from states $|0, 1, 1\rangle$, $|0, 2, \{2, 1, 0\}\rangle$ to states $|1, 0\rangle$, $|1, 1, \{1, 0, -1\}\rangle$ respectively. A third laser, linearly polarized with higher frequency excites the population in $|0, 0\rangle$ to $|1, 1, 0\rangle$. Subsequent infrared decays by virtue of selection rules, $\Delta J = \pm 1$ and $\Delta M_J = 0, \pm 1$ effectively transfer the populations from the above states to a single state $|0, 1, 0\rangle$ (referred as $|g0\rangle$). The empty states of $|1, 1, \pm 1\rangle$ are referred as $|g\pm\rangle$. The $\sigma^+$ and $\sigma^-$ polarized lasers are switched on alternatively instead of simultaneously to avoid the creation of a dark state which will prevent complete pumping to state $|g0\rangle$. Taking into account the magnetic levels splitting by the trapping field and small differences in the rovibrational transition frequencies, we could use the lasers with a finite bandwidth to resonantly excite all the above transitions near the trap center. The pumping process takes about $5\tau_{IR} \approx 0.05 s$ ($\tau_{IR}$ is the IR natural lifetime) which is considerably shorter than a typical trapping lifetime (for example CaH lifetime is about $0.6 s$ [7]).

Even after rotational pumping, there is a small fraction of the molecules remaining in higher vibrational and rotational states. These molecules are not in the 4 cooling cycle state ($|g0\rangle$, $|g\pm\rangle$ and $|e\rangle$). Therefore, they will not be translationally cooled and can be disregarded. Among these 4 states, only a single state $|g0\rangle$ is populated while the rest are essentially empty within a rovibrational decay lifetime. Thus, we still have a large fraction of buffer gas cooled thermal molecules in a single internal state $|g0\rangle$ as the precursor for translational cooling. When the trapping field is switched off, the laser cooling starts.

IV. ESTIMATION OF COOLING PARAMETERS

We show that the propose cooling scheme can be realized in practice. Based on the results of our theoretical studies, we use realistic physical parameters to briefly estimate the cooling time for each step. It is essential to have a short total cooling time for unconfined cooling so that the molecules are cooled before they fly apart beyond the laser cooling region. Once translationally cooled, the molecules can be easily manipulated and confined in a simple and shallow trap.

A. Velocity selection

The velocity selected momentum width can be arbitrarily narrow using long duration Raman $\pi-$pulses. For practical purpose, it is essential to consider an optimum pulse duration for this step. Since the selected population is shifted by discrete number of $h(k_- + k_+) \approx 2h\lambda$ in the deceleration step, it is most efficient to have the selected width of $\Delta P_{vs} \approx 2h\lambda$, corresponding to 4 times the recoil temperature, which is $T_{vs} = \frac{(2\hbar k)^2}{M} \approx 4\mu K$ for optical wavelength of $\lambda = 300 nm$ and molecular mass of $M = 100 a.m.u$. For Blackman pulse shape [9], the required $\pi-$pulses duration is estimated to be $\tau_1 \approx \frac{16M}{k M_{IR}} = \frac{15}{k^2 \tau_{IR}} \approx 27 \mu s$, which is longer than the natural lifetime ($\Gamma_c \approx 10^7 s^{-1}$) of state $|e\rangle$ and the vibrational period of a molecule [16]. Since the sweep of the Blackman pulses is not a rapid passage, the excited state will be appreciably populated unless the optical detuning $\delta$ is large enough, but smaller than the rotational level spacing (around $10^{10} s^{-1}$) to avoid excitations to untargeted rotational states. We use $\delta = -50\Gamma \approx 5 \times 10^8 s^{-1}$. The corresponding Rabi frequency amplitude is $\Omega_o = \sqrt{-\delta\tau_1/(\tau_0 0.61)} \approx 9.8 \times 10^8 s^{-1}$ [17].

For a molecular gas of mass $100 a.m.u.$ and initial temperature $T_i = 1 K$, the momentum width is the maximum mean momentum is taken to be $P_{max} = \sqrt{2M k_B T_i} \approx 1000 h k$. If each velocity selection step selects a momentum width of $\Delta P_{vs} = 2h\lambda$, the total number of velocity selection steps which is the number of cooling cycle, $N_{max} = 2P_{max}/\Delta P_{vs} \approx 1000$, The total time required for velocity selection in the cooling process is $t_1 = N_{max} \tau_1 \approx 27 ms$.

B. Deceleration

For complete population transfer between states $|g+\rangle$ and $|g-\rangle$ in each STIRAP inversion, in addition to counterintuitive sequence and overlapping pulses, the pulses duration $\tau_2$ must meet the adiabatic criteria [18]. Our simulations which take into account spontaneous emissions using master equations give a criteria of $\tau_2 \Omega_o \gtrsim 50$ for 99.95% transfer efficiency with zero detuning. With an efficiency of $\epsilon = 99.95\%$ for each STIRAP inversion, the minimum deceleration efficiency corresponds to the maximum number of inversions $N_{max} = 1000$ for molecules with mean $P_{N_{max}}$, which is $\epsilon_N = \epsilon N_{max} = 60\%$. 

4
In one-photon resonant condition to intermediate state $|e\rangle = |X, n = 0, J = 0, M_J = 0\rangle$, the finite spectral width $\Delta \omega$ of the pulses must be much smaller than rotational level spacing $\omega_{rot}$ to avoid off-resonant coupling to additional intermediate states which may lead to imperfect transfer efficiency; for example, $\Delta \omega \approx 1/\tau_2 << \omega_{rot} \approx 10^{10} s^{-1}$. Thus, one can safely use the typical [18] nanosecond STIRAP pulses and have each inversion duration of $t_3$ is estimated as $t_3 \approx N_{max} \Delta \omega^{-1} \approx \tau_3 \approx 1 ms$. The total deceleration time in the cooling process is estimated as

$$t_2 = \sum_{N=1}^{N_{max}} N_{max} = \sum_{N=1}^{N_{max}} N \tau_2 = \frac{1}{2} N_{max} (N_{max} + 1) \tau_2 \approx 5 ms$$

Despite the large number of STIRAP inversions, the total cooling time in step 2 is still less than the total time for velocity selection.

C. Accumulation

In practice, the decelerated molecules in $|g+\rangle$ or $|g-\rangle$ can be driven resonantly by c.w. laser to an excited electronic state for fluorescence decay to many ground rovibrational levels within $\tau_3 = 10/\Gamma_e \approx 1 \mu s$. The total accumulation time is $t_3 \approx N_{max} \tau_3 \approx 1 ms$. Thus, the total time for the whole cooling process is $t_{cool} = t_1 + t_2 + t_3 \approx 33 ms$. The cooling can be done simultaneously on the positive and negative sides of the momentum distribution. If the velocity selection and deceleration start from the fastest molecules to the slowest, the drift distance for molecules with momentum $P$ can be done simultaneously on the positive and negative sides of the momentum distribution. If the velocity selection is optimized by minimizing the order of velocity selection on certain velocity class.

V. MODELLING OF THE COOLING EFFECT

A. Initial state and density matrices

From the practical descriptions in Section III, we assume that initially the internal state is pure and uncorrelated to the center of mass momentum state. Only the internal state $|g0\rangle$ is occupied. The center of mass subsystem is in the thermal Gibbs state [20] and the initial total density operator is written as

$$\hat{\rho}_{tot}(0) = \hat{\rho}_I(0) \otimes \hat{\rho}_{cm}(0) = |g0\rangle \langle g0| \otimes \sum_P W(P) |P\rangle \langle P|$$

where $W(P) = \frac{1}{Z} e^{-P^2/\sigma^2}$ is the statistical weight, $Z = \sum_P e^{-P^2/\sigma^2}$ is the partition function and $\sigma = \sqrt{2MK_BT}$ is the initial momentum width with effective temperature $T$. On one hand the gas is coupled to lasers, while on the other hand it forms an open system whereby it can exchange entropy with the outside environment.

The quantum dynamical evolution of the molecules in each cooling step and throughout the cooling process can be modeled analytically by using the density matrix elements. This enables convenient evaluation of the internal and center of mass subsystems probability distributions and the corresponding entropies, which allow us to work out the dynamics and the cooling efficiency. The density matrices of the total system, internal subsystem and center of mass subsystem in internal basis $\{|a\rangle\}$ and center of mass momentum basis $\{|P\rangle\}$, are defined respectively as

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

$$\hat{\rho}_I(t) = Tr_{cm} \{\hat{\rho}_{tot}(t)\} = \sum_{a,b} |a\rangle \langle b| \sum_P \rho_{ab}(P,P,t)$$

$$\hat{\rho}_{cm}(t) = Tr_I \{\hat{\rho}_{tot}(t)\} = \sum_{P,P'} |P\rangle \langle P'| \sum_a \rho_{aaa}(P,P',t)$$
where \( \rho_{ab}(P, P', t) \equiv \langle a, P|\hat{\rho}_{tot}(t)|b, P' \rangle \) are the total system density matrix elements, \( a, b \in \{ e, g0, g1, g2, g3, d, \{\text{acc}_j\}\} \) the internal states and \( \{ P, P' \} \) the center of mass 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 [7]. 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 center of mass coherences in the populations, for example \(|g+, P - \hbar k\rangle|g+, P - 3\hbar k\rangle\), are negligibly small. We start with populations in the internal state \(|g0\rangle\) and the center of mass Gibbs state with no coherences in momentum basis. 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 center of mass 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, transitions between different internal states are accompanied by momentum recoil. Thus, the matrix elements between different internal states \( (a \neq b) \) are non vanishing only for the center of mass coherences \( P \neq P' : \rho_{ab}(P, P', t) \neq 0 \) and \( \rho_{ab}(P, P, t) = 0 \). Accordingly, Eqs. (3) and (4) reduce to

\[
\hat{\rho}_I(t) = \sum_a C_a(t)|a\rangle\langle a| \\
\hat{\rho}_{cm}(t) = \sum_P f(P, t)|P\rangle\langle P| 
\]

where the internal and center of mass probability distributions \( C_a(t) \) and \( f(P, t) \) are respectively defined as

\[
C_a(t) = \sum_P \rho_{aa}(P, P, t) \\
f(P, t) = \sum_a \rho_{aa}(P, P, t) 
\]

Thus, we only need to evaluate the diagonal density matrix elements \( \rho_{aa}(P, P, t) \) in order to calculate the subsystem density matrices and the corresponding entropies.

VI. POPULATION DYNAMICS

1. Step 1 of \( N\)-th cooling cycle: To simplify the mathematics, we can model the velocity selected momentum distribution by a Gaussian function of a narrow width \( \sigma_{\text{vsel}}(<< \sigma) \). During step 1 of the \( N\)-th cooling cycle (subscript \( N:1 \)), only the populations in the states \(|g0\rangle\) and \(|g+\rangle\) change with time and can be written analytically as the following:

\[
\rho_{00}(P, P, t_1)_{N:1} = W(P) - \sum_{j=1}^{N-1} V_j(P) - V_N(P)h_1(t_1) \\
\rho_{++}(P, P, t_1)_{N:1} = h_1(t_1)W(P)N)e^{-(P+\alpha\hbar k_{N,+}-P_N)^2/\sigma_{\text{vsel}}^2} 
\]

where \( 0 \leq t_1 \leq \tau_1 \). \( \tau_1 \) is the duration of the population transfer in step 1. The function \( h_1(t_1) = \sin^2\pi t/2\tau_1 \) describes the time evolution of the populations. \( V_j(P) = W(P) e^{-(P-P_j)^2/\sigma_{\text{vsel}}^2} \) is the velocity selected distribution in the \( j\)-th \((j = 1... N)\) cooling cycle with mean momentum \( P_j \), momentum width \( \sigma_{\text{vsel}} \) and mean population \( W(P_j) = \frac{2\pi e^{-P_j^2/\sigma_{\text{vsel}}^2}}{\sigma_{\text{vsel}}^2} k_{N,+} \) is the \( \sigma^+ \) laser wavevector of the \( N\)-th cooling cycle and \( \alpha = \text{sign}(P_j) \) determines the direction of the \( \sigma^+ \) laser to provide decelerating momentum kick.

The first term in Eq. (9) describes the initial populations distribution. The second term corresponds to the depleted populations after \( N - 1 \) cooling cycles. The third term describes the transient population depletion in the \( N\)-th cooling cycle. In the end of step 1, the populations become

\[
\rho_{00}(P, P, \tau_1)_{N:1} = W(P) - \sum_{j=1}^{N} V_j(P) \\
\rho_{++}(P, P, \tau_1)_{N:1} = W(P)N)e^{-(P+\alpha\hbar k_{N,+}-P_N)^2/\sigma_{\text{vsel}}^2} 
\]
Step 2 of N-th cooling cycle: There are many substeps within step 2. Only the populations in states $|g+\rangle$ and $|g-\rangle$ change with time during the $n$-th substep of step 2 in the N-th cooling cycle, according to

$$\rho_{aa}(P, P, t_2)_{N:2(n)} = h_2(t_2)W(P_N)e^{-(P+\alpha \hbar k_{N,+}+\alpha \Lambda_n-P_N)^2/\sigma_{vsel}^2}$$ (15)

$$\rho_{bb}(P, P, t_2)_{N:2(n)} = (1-h_2(t_2))W(P_N)e^{-(P+\alpha \hbar k_{N,+}+\alpha \Lambda_n-1-P_N)^2/\sigma_{vsel}^2}$$ (16)

$$\rho_{++}(P, P, 0)_{N:2(1)} = \rho_{++}(P, P, \tau_1)_{N:1}$$ (17)

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 $0 \leq t_2 \leq \tau_2$, each with the same duration $\tau_2$ for complete inversion. $h_2(t_2) = \sin^2 \pi t/2\tau_2$ describes the time evolution of the populations and $\Lambda_n \equiv \sum_{j=1}^{m} h(k_j+1-k_j) \approx 2n\hbar k$ is the total amount of momentum transfer provided by $n$ pairs of STIRAP pulses. The precise values of $k_{N,+}$, $k_{j,+}$ and $k_{j,-}$ are obtained via the two-photon Raman resonance condition. In the numerical simulations they are simply taken to be approximately equal to $k$ without affecting the validity of the results.

The momentum width $\sigma_{vsel}$ is unchanged throughout step 2. The number of deceleration cycles $n_{\text{max}}$ required to reduce the mean momentum from $P_N$ to zero can be predicted through $\alpha \hbar k_{N,+}+\alpha \Lambda_n-P_N \approx \alpha \hbar k(1+2n_{\text{max}})-P_N \approx 0$, which gives

$$1 \leq n \leq (n_{\text{max}} = \frac{P_N}{2\alpha \hbar k} - \frac{1}{2}).$$ (18)

In the end of step 2, the populations become

$$\rho_{aa}(P, P, \tau_2)_{N:2(n_{\text{max}})} \approx W(P_N)e^{-\vec{P}^2/\sigma_{vsel}^2}$$ (19)

Step 3 of N-th cooling cycle: After step 2, if the cooled populations from the Raman states $|g\pm\rangle$ are transferred rapidly to the decaying state $|d\rangle$ with a short $\pi$-pulse, the process is essentially unitary due to negligible spontaneous emissions from $|d\rangle$. Furthermore, if the laser is orthogonal to the $z$-direction, no momentum kick is imparted in $z$-direction. This enables the replacement $\rho_{dd}(P, P, 0)_{N:3} \approx \rho_{aa}(P, P, \tau_2)_{N:2(n_{\text{max}})}$ as initial population, setting $\rho_{++}(P, P, t_3)_{N:3} = 0$ and disregarding the dynamics of the $\pi-$pulse. The population in $|d\rangle$ decay to many vibrational-rotational levels in the ground electronic state. 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 $\{|\text{acc}_j\rangle, j = 1...M\}$ with the corresponding decay rates $\Gamma_j$. This is given by

$$\rho_{dd}(P, P, t_3)_{N:3} = \sum_{j=1}^{M} F_j e^{-\Gamma_j t_3}W(P_N)e^{-\vec{P}^2/\sigma_{vsel}^2}$$ (20)

$$\rho_{\text{acc}_j}(P, P, t_3)_{N:3} = F_j \frac{\sigma_{\text{vsel}}}{\sigma_{\text{acc}}} e^{-\vec{P}^2/\sigma_{\text{vsel}}^2} \{ \sum_{j=1}^{N-1} W(P_j) + W(P_N)(1-e^{-\Gamma_j t_3}) \}$$ (21)

where $0 \leq t_3 \leq \tau_3$ is the time interval for step 3, $\tau_3$ 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 $|\text{acc}_j\rangle$ with $\sum_{j=1}^{M} F_j = 1$.

The first term in the curly bracket of Eq. (19) corresponds to the cumulative populations from the previous $N - 1$ cooling cycles. It is equal to the depleted populations from $|g0\rangle$ while the second term describes the transient increase in populations. The accumulated momentum width $\sigma_{\text{acc}}$ is slightly larger than $\sigma_{\text{vsel}}$ due to the small momentum spread (about $0.5\hbar k_a$) from a single spontaneous emission. The normalization factor $\frac{\sigma_{\text{acc}}}{\sigma_{\text{vsel}}}$ in Eq. (19) ensures that $Tr_{\text{tot}}\{\hat{\rho}_{\text{tot}}\} = 1$ and can be estimated by

$$\sigma_{\text{acc}}/\sigma_{\text{vsel}} \approx 1 + 0.5\hbar k_a/\sigma_{\text{vsel}}$$ (22)

where $k_a = (E_d - E_{\text{acc}})/\hbar c$.

VII. ENTROPIES

The cooling effect is shown by the variation in the momentum probability distribution and the variations of the total, internal and center of mass von Neumann entropies $[19]$. From Eq. (1) the initial internal, center of mass and total entropies are respectively:
\[ S_I(0) = 0 \]  
\[ S_{cm}(0) = -k_B \sum_P W(P) \ln W(P) \]  
\[ S_{tot}(0) = S_{cm}(0) \] (25)

The expressions for internal and center of mass entropies are obtained from Eqs. (5)-(8) using \( S_X(t) = Tr\rho_X(t) \ln \rho_X \) where \( X \in \{I, cm\} \), as follows:

\[ S_I = -k_B \sum_a C_a \ln C_a \] (26)

\[ S_{cm} = -k_B \sum_P f(P) \ln f(P) \] (27)

Equations (24) and (25) are valid for all times in all cooling steps and take a simple form because the reduced density matrices are diagonal (Eqs. (5) and (6)). The center of mass probability distributions for step 1, 2 and 3 of the \( N \)-th cooling cycle are given by:

\[ f(P, t_1)_{N:1} = \sum_{a=0,+} \rho_{aa}(P, P, t_1)_{N:1} + \sum_j \rho_{acc_j}(P, P, \tau_3)_{(N-1):3} \] (28)

\[ f(P, t_2)_{N:2(n)} = \rho_{00}(P, P, \tau_1)_{N:1} + \sum_{a=+,-} \rho_{aa}(P, P, t_2)_{N:2(n)} + \sum_j \rho_{acc_j}(P, P, \tau_3)_{(N-1):3} \] (29)

\[ f(P, t_3)_{N:3} = \rho_{00}(P, P, \tau_1)_{N:1} + \rho_{dd}(P, P, t_3)_{N:3} + \sum_j \rho_{acc_j}(P, P, t_3)_{N:3} \] (30)

Using \( \int_{-\infty}^{\infty} e^{-(P-a)^2/\sigma_v^2} dP = \sigma_v \sqrt{\pi} \), we can show that \( f(P) \) is normalized. \( \int f(P)dP = 1 \). Similarly, the internal probability distributions for step 1, 2 and 3 of the \( N \)-th cooling cycle are given by:

\[ C_{0,+(t_1)_{N:1}} = \sum_P \rho_{00,++}(P, P, t_1)_{N:1} \]  
\[ C_{acc_j(t_1)_{N:1}} = \sum_P \rho_{acc_j}(P, P, \tau_3)_{(N-1):3} \] (31)

\[ C_{0(t_2)_{N:2(n)}} = \sum_P \rho_{00}(P, P, \tau_1)_{N:1} \]  
\[ C_{+,-(t_2)_{N:2(n)}} = \sum_P \rho_{++,--}(P, P, t_2)_{N:2(n)} \]  
\[ C_{acc_j(t_2)_{N:2(n)}} = \sum_P \rho_{acc_j}(P, P, \tau_3)_{(N-1):3} \] (32)

\[ C_{0(t_3)_{N:3}} = \sum_P \rho_{00}(P, P, \tau_1)_{N:1} \]  
\[ C_{d(t_3)_{N:3}} = \sum_P \rho_{dd}(P, P, t_3)_{N:3} \]  
\[ C_{acc_j(t_3)_{N:3}} = \sum_P \rho_{acc_j}(P, P, t_3)_{N:3} \] (33)

The total density matrix in this step involves the basis states \( |g0\rangle, |d\rangle \) and \( \{|acc_j\}\}. It is diagonal since these states are not coupled by laser. The evolution is characterized by free spontaneous emission from \( |d\rangle \) to \( \{|acc_j\}\}. Thus, the time evolution of the total density matrix for step 3 can be written in a completely diagonal form

\[ \dot{\rho}_{tot}(t_3)_{N:3} = \sum_P \rho_{00}(P, P, \tau_1)_{N:1} |0, P\rangle \langle 0, P| + \sum_{a=d,\{acc_j\}} \rho_{aa}(P, P, t_3)_{N:3} |a, P\rangle \langle a, P| \] (34)

with \( Tr_{tot}\{\dot{\rho}_{tot,N}(t)\} = 1 \).
The total entropy changes only during incoherent process in step 3. Its time evolution in the \( N \)-th cooling cycle is given by

\[
S_{tot}(t_3)_{N:3} = -k_B \sum_{P} \{ \rho_{00}(P, P, \tau_1)_{N:1} \ln \rho_{00}(P, P, \tau_1)_{N:1} + \sum_{a=d,\{acc\}} \rho_{aa}(P, P, t_3)_{N:3} \ln \rho_{aa}(P, P, t_3)_{N:3} \} \tag{35}
\]

Throughout the coherent interactions of step 1 and step 2 in the \( N \)-th cooling cycle, the total entropy takes a constant value of \( S_{tot}(t_3)_{(N-1):3} \).

Each cooling cycle is completed in step 3, during which radiation entropy \( S_R(t) \) 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. From the knowledge of the angular distribution of the spontaneously emitted photons, we can write the radiation density matrix as

\[
\hat{\rho}_R = \frac{1}{2\pi} \sum_{j, \lambda} \int_{0}^{2\pi} \int_{0}^{\pi} F_j M_\lambda(\theta) |j, \lambda, \theta, \phi\rangle \langle j, \lambda, \theta, \phi| \sin \theta d\theta d\phi
\]

where \( |j, \lambda, \theta, \phi\rangle \) is the state of the photon emitted with frequency \( \omega_{acc} = (E_d - E_{acc}) / \hbar \), polarization \( \lambda = 0, \pm 1 \), and in spherical coordinate angles \( (\theta, \phi) \) relative to the dipole axis. \( M_\lambda(\theta) = \frac{1}{2}(1 + \cos^2 \theta) \delta_{\lambda, \pm 1} + \frac{1}{2} \sin^2 \theta \delta_{\lambda, 0} \) corresponds to the probability of emission at angle \( \theta \) relative to the dipole axis and \( F_j \) is the Franck-Condon factor. The trace over all decay frequencies and angles gives \( T\rho_{j,\lambda,\theta,\phi} \rho_R \) = 1. The radiation entropy corresponding is easily obtained as

\[
S_R(t) = -k_B \sum_{j, \lambda} \int_{0}^{\pi} R_{j,\lambda,\theta} \ln R_{j,\lambda,\theta} d\theta \tag{37}
\]

where \( R_{j,\lambda,\theta} = F_j M_\lambda(\theta) \sin \theta \).

We note that the existence of many \( |acc\rangle \) states during step 3 leads larger radiation entropy due to the frequency dispersion, in addition to the angular dispersion of the spontaneously emitted photons.

**VIII. RESULTS AND DISCUSSIONS**

Based on the model discussed above, we simulate the essential features of the cooling process. The typical variations of the internal populations distribution for each step in a cooling cycle is shown in Figs. 3. In each cooling cycle, a fraction of molecules with a narrow momentum width are depleted from the state \( |g0\rangle \) by velocity selection (Fig. 3a), slowed towards zero mean momentum via repeated inversion by STIRAP (Fig. 3b) and dumped irreversibly into the accumulation states (Fig. 3c).

We give the overall results of the cooling process first and discuss the details of the cooling mechanism later. The cooling effect is shown by the narrowing of the momentum probability distribution \( f(P) \), which evolves from a large momentum width (about \( 30\hbar k \)) into a narrow momentum width (about \( 2\hbar k \)) with zero mean momentum (Fig. 6). The main interest of this paper is the center of mass entropy \( S_{cm} \) which is found to decrease after the cooling process (Fig. 5a), 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 cooling in the molecular translational degree of freedom. The coherent processes of steps 1 and 2 contribute substantially to the reduction of \( S_{cm} \), from the maximum entropy of Gibbs state to the final populations with narrow momentum width. Throughout the cooling, the internal entropy \( S_I \) increases(Fig. 5a). Within each cooling cycle, the laser fields have created correlations between internal and center of mass momentum states, thus transferring the entropy from the center of mass to the internal subsystems by reducing the center of mass state dispersion while increasing the internal state dispersion. Indefinite repetition of the center of mass cooling effect is possible through the irreversible process of step 3.

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 center of mass states. During velocity selection, the extraction of a narrow slice of momentum from \( |g0\rangle \) leads to distortion in the momentum distribution. One \( \hbar k \) of momentum kick on the velocity selected population leads to a narrower overall momentum distribution and to the reduction of \( S_{cm} \)(Fig. 4a). At the same time, \( S_I \) increases(Fig. 4b) because an additional internal state \( |g+\rangle \) is increasingly populated.

In the deceleration step, \( S_{cm} \) is reduced in each substep (Fig. 4a) by repeated momentum kicks which push the selected populations closer to zero mean momentum. Entanglement [21] of the center of mass momentum states in each
STIRAP process increases the population dispersion of the center of mass states. This explains the transient increase in $S_{cm}$, which is less than the overall reduction of $S_{cm}$ 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 $S_{cm}$. The first STIRAP process reduces $S_{cm}$ more than the subsequent ones. This quantitative difference is due to the nonlinear dependence of the entropy on the momentum distribution. However, $S_I$ oscillates above a constant value (Fig. 4b). Each oscillation corresponds to a substep, which is an inversion process by STIRAP and can be explained by the creation of adiabatic states through the entanglement of states $|g+\rangle$ and $|g-\rangle$. The entanglement involves the population of an additional internal state, thereby increasing $S_I$. After the completion of a STIRAP process, the entanglement disappears and $S_I$ falls back to the value before the entanglement. Thus, the value of $S_I$ before and after step 2 are the same.

The total entropy $S_{tot}$ is constant throughout steps 1 and 2 but changes only during step 3 (Fig. 4c). This shows that unitary evolution can reduce the center of mass entropy despite the invariance of the total entropy. In other words, coherent interaction alone is able to cool the center of mass subsystem at the expense of heating the internal subsystem. However, the cooling cannot be repeated unless an irreversible process is introduced as part of the cooling cycle, which is step 3. In step 3, the slight increase in $S_{cm}$ due to momentum spread from one spontaneous emission is smaller than the decrease in $S_{cm}$ in steps 1 and 2 (Fig. 4a). This leads to the overall reduction of $S_{cm}$ in each cooling cycle. In fact, it is the coherent process of steps 1 and 2 instead of the spontaneous emission, which substantially reduces $S_{cm}$. This is an essential point, as it indicates that coherent process can lead to substantial change in the subsystem entropy. The important role of the single spontaneous emission is to irreversibly accumulate the translationally cooled populations. We note that this accumulation role can also be realized if the cooled populations in each cooling cycle are coherently transferred to different internal (acc) states. For this, the number of (acc) states has to be more than the number of cooling cycles and multi-frequency lasers resonant with all the (acc) states would be required. In this case, the whole cooling process is coherent and no spontaneous emission is required. Then, both translational and internal cooling cannot be achieved simultaneously. Translational cooling must be accompanied by internal heating, or vice versa. Thus, coherent cooling of translational motion is not a conceptual impossibility but rather a practical one, at least at the present moment.

The entropy variations for a single (acc) state and multi (acc) states are shown in Fig. 4b and Fig. 4c (we use 10 (acc) states with logarithmic Franck-Condon factors and a fixed decay rate). With single (acc) state, $S_I$ 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)) to two states ($|g0\rangle$, (acc))(Fig. 4b). The center of mass entropy $S_{cm}$ is unaffected by the number of (acc) states (Fig. 4a). However, the internal entropy $S_I$ increases with more (acc) states since the number of populated internal states increases (Fig. 4b). It is interesting to observe that the increase in $S_I$ from populating 10 internal states (in step 3) is still smaller than the increase in $S_I$ 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.

The internal and center of mass entropies fluctuate throughout the cooling process (Fig. 5a). As the momentum width of the populations shrinks towards a narrow velocity selected width in the cooling process, the $S_{cm}$ reduces from the maximum entropy state towards zero. The small residual populations in the right and left wings of the narrow peak (Fig. 6) 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 $S_{cm}$ closer to zero in the end of the cooling process. On overall, $S_I$ increases in every cooling cycle due to the increase of the populations in the many (acc) states, thus changing from populating an internal state $(S_I = 0)$ to populating multi internal (acc) states.

The total entropy $S_{tot}$ before and after the cooling do not seem to change a lot (Fig. 5b). In fact, $S_{tot}$ can increase or decrease due to the coupling of the total system to the environment. The total, internal and center of mass entropies satisfy the Araki-Lieb inequality [22], $|S_I - S_{cm}| \leq S_{tot} \leq S_I + S_{cm}$, as shown in Fig. 4c and 5b. Therefore, the cooling results are consistent with the general properties of quantum entropy. The non-negligible index of correlation $I_C = S_{cm} + S_I - S_{tot}$ [20] shows that the internal and center of mass subsystems are correlated by the laser interactions throughout the cooling process. However, after cooling the correlation is not maximum since $S_{tot}$ is not zero and $S_{cm} \neq S_I$.

We note that the increase in the internal entropy is due to the specific choice of the accumulation scheme (step 3), due to practical requirement for faster cooling time. The amount of increase in the internal and radiation entropies depend essentially on the number of (acc) states. The resulting internal heating is entirely analogous to creation of radiation entropy. The many internal states in molecules provide an additional entropy sink, much like the radiation Fock states. During the cooling process, the translational entropy is removed irreversibly by spontaneous emissions to these entropy sinks.

If we had coherently accumulated the cooled molecules by transferring each cooled fraction of molecules after each
cooling cycle to distinct rovibrational states instead of using spontaneous emission, less radiation entropy will be created while the internal entropy increases dramatically. This requires multi-frequency lasers, which may not be practical. On the other hand, we can use a low rovibrational state as \( |d\rangle \) state which has less decay channels. Then, infrared (IR) spontaneous emission will be the accumulation mechanism instead of optical spontaneous emission and the radiation entropy would still increase but with less populated \( |\text{acc}\rangle \) states and therefore less internal entropy. However, the long IR decay lifetime leads to longer cooling time.

The model presented above does not consider further IR decays from the \( |\text{acc}\rangle \) states to lower rovibrational states. Within about 0.1s, the molecules essentially end up in the ground vibrational state by multiple IR decays. Thus, the vibrational heating occuring in the model is a transient effect. We have shown the model up to a stage where translational cooling has been achieved to a large extend, which is the aim of our cooling scheme. To summarize, the resulting internal heating is not a practical concern in this work since our aim is translational cooling. Translationally cooled molecules (even if internally hot) are invaluable assets in many fundamental and applied sciences.

**IX. CONCLUSIONS**

We have developed a laser cooling concept for translational motion of neutral molecules based on the repetition of three steps: velocity selection, deceleration and accumulation by a single spontaneous emission per molecule. Each molecule need not undergo repeated spontaneous emissions to be translationally cooled. Using realistic cooling parameters, we have estimated the cooling time, which turns out to be practically feasible to cool down thermal molecules of 1K to around recoil width. We have modelled the cooling process and studied the changes in the entropies. Simulations of the model have shown the reduction of the momentum width and the center of mass entropy by the cooling process. The many internal states of molecules can serve as a useful entropy sink, in addition to the radiation entropy for translational cooling. Analysis has shown that our scheme to translationally cool molecules by lasers, can be realized in principle and in practice. This cooling concept should open up a new possibility for translational laser cooling of molecules.

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FIG. 1. A rotational pumping scheme for initial state preparation
FIG. 2. Schematic diagrams for each cooling cycle composed of 3 sequential steps: a) narrow velocity width selection, b) deceleration of selected molecules and c) accumulation of decelerated and narrow momentum width molecules by a single spontaneous emission to one of the many accumulation states.
FIG. 3. Momentum distributions of the internal populations in a typical cooling cycle after the steps of: a) velocity selection, b) deceleration and c) accumulation.
FIG. 4. Evolution of the a) center of mass entropy $S_{cm}$, b) internal entropy $S_I$, and c) total entropy $S_{tot}$ as well as $S_{cm} \pm S_I$ 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.
FIG. 5. Results after the whole cooling process with 10 accumulation states for a) $S_{cm}$ and $S_I$, b) $S_{tot}$ and $S_{cm} \pm S_I$. 
FIG. 6. Total momentum probability distribution $f(P)$ before and after the cooling process.
Figure 2

Figure 3
Figure 4
Figure 5
Figure 6

Before cooling

After cooling