Density and phase-space compression of molecular gases in magneto-electrostatic traps

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We introduce, analyze, and compare two methods of single-photon cooling that generically cool and compress molecular gases. The first method compresses the molecular gas density by 3 orders of magnitude and increases collision frequency in trapped samples. The second method compresses the phase-space density of the gas by at least 2 orders of magnitude. Designed with combinations of electric and magnetic fields, these methods cool the molecules from ∼100 to 1 mK using a single irreversible state change. They can be regarded as generic cooling schemes applicable to any molecule with a magnetic and electric dipole moment. The high efficiency calculated, compared to schemes involving cycling, is a result of cooling the molecules in a single step.

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I. INTRODUCTION

For many years, the scientific community has been striving to develop general methods of molecular and atomic cooling for the fields of cold chemistry and physics. This ability would open the door to many different experimental categories, such as the observation of chemical reactions in uncharted temperature regimes, observation of Bose-Einstein Condensation in a wide variety of molecular and atomic species, and quantum computing [1]. Such a source would allow for a great increase in the precision of molecular spectroscopy and measurements of fundamental constants [2,3]. In the cold-temperature regime (below 1 K), the de Broglie wavelength is on the order of the interaction potential where quantum effects should dominate, yet this regime is largely unmeasured even though many theoretical predictions exist [4–6]. Indeed, the ultracold regime below 1 mK where quantum degenerate molecular gases can form, is even more mysterious and unexplored [7].

Sources of cold molecules (∼10^{-3}–10^{-2} mK) have existed for many years, such as cooling via supersonic expansion [8] or cooling via collisions (buffer-gas cooling) [9], yet observations of chemical reactions below 1 K have been limited to charged or laser-cooled species. Supersonic expansion creates cold beams (∼100 mK), which due to enthalpy conservation, travel at supersonic velocities. Many methods to slow these beams have been explored, such as Stark deceleration [10–12], Zeeman deceleration [13,14], optical deceleration [15], and mechanical deceleration [16,17]. However, the resulting particle density is too low to observe chemical reactions. Recently, we have developed a comoving magnetic trap, which utilizes the Zeeman effect in a three-dimensional moving magnetic trap to slow any type of particle that has a magnetic dipole moment without compromising the density or temperature removing over 98% of the kinetic energy [18,19].

The ultracold regime has been reached with a very specific set of atomic and molecular gases. The original method used to reach this regime was laser cooling, which was developed over a decade and a half ago. When combined with evaporative cooling, it can effectively cool specific atomic species to the nanokelvin range. Direct laser cooling on molecules is a difficult task because of the complexity of the molecular structure and the absence of lasers at the required wavelengths. It is possible to find specific molecules that have particularly favorable Franck-Condon transition factors such that direct laser cooling can be performed as was demonstrated by the DeMille group with SrF [20]. Currently, the most successful methods for molecular cooling to the ultracold regime are atomic-based techniques in which atoms are cooled to the nanokelvin range and then are combined via photoassociation [21,22] or Feshbach resonances [23,24] to form molecules without heating. These methods create the coldest molecular gases to date but are not general as they are limited to atomic precursors that are amenable to laser cooling. Other approaches include cycling the molecules between the vibrational and the rotational states removing energy with every cycle in a Sisyphus-type scheme as proposed by Pritchard [25]. The difficulty in such a method is finding a closed cycle within the complexity of the molecular structure by managing all of the allowed transitions. The Rempe group has demonstrated that this is feasible in an experimental implementation of such a cycling scheme, cooling a molecular gas of CF$_3$H from 100 to 1 mK in about 10 s [26], which is on the order of magnitude of the lifetime of the trap. The importance of reaching the 1-mK threshold is that, at this temperature, loading of the gas into an optical dipole trap should be possible allowing further cooling by evaporative cooling. This is necessary since evaporative cooling in an electrostatic and magneto-static trap is not possible due to state-changing collisions [27]. Finally, an irreversible loading step can be used in order to accumulate molecules in a static trap as proposed and implemented in Riedel et al. [28] and van de Meerakker et al. [29].

The purpose of the methods introduced in this paper is to efficiently and generically cool a molecular sample, entrained in a supersonic beam and slowed by the comoving magnetic trap decelerator from ∼100 mK to any desired value above 1 mK. These methods are tools for the exploration of this range and for the eventual loading of the gas into an optical dipole trap with higher efficiencies than those demonstrated to date. Both methods are based on single-photon cooling (SPC), which was introduced and was implemented for Rb atoms in Price et al. [30]. The Steck group has also implemented a Maxwell’s demon–based method to cool atoms using a one-way optical barrier [31], which was proposed in Raizen et al.

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The problem in the direct application of SPC to molecules is that the polarizability of small radicals is usually too low, and high laser power (∼1 kW) is needed in order to create adequately deep optical dipole traps. Even with such high laser power, the efficiency of SPC into an optical dipole trap would be low (∼10⁻⁵) due to the small phase space in comparison to the initial sample phase-space density.

II. SINGLE-PHOTON COOLING

In SPC, particles are irreversibly transferred from one state to another around the particles’ classical turning point, changing their effective potential surfaces. SPC takes advantage of the kinetic-energy exchange with the conservative potential energy to lower the particle’s total energy. The kinetic energy of such a particle remains the same while it is trapped in a different potential surface according to the new state of the particle. It will be shown that a large tunable fraction of the total energy can be removed in such a process. The OH radical in the ²Π₃/₂ electronic ground state will be used as a practical example. The total angular momentum of the OH radical in the ground state is J = 3/2. There are four Zeeman sublevels with different projections of the total angular momentum on the quantization axis as displayed in Fig. 1.

Assume that the process begins with a cloud of cold OH radicals in the fully stretched m₁ = 3/2 state. Suppose now that we irreversibly transfer a “hot” molecule at the classical turning point from the m₁ = 3/2 into the m₁ = 1/2 Zeeman sublevel (see Fig. 1). This process reduces the total energy of the molecule by a factor of 3, given by the slope ratio between the two potential surfaces. In order to remove a substantial amount of energy, one needs to repeat this cycle many times, greatly increasing the time scale of the process and lowering its efficiency. Clearly, the molecular structure, which includes vibrational rotational hyperfine energy levels, complicates the possibility of cycling.

III. SPC UTILIZING A MAGNETO-ELECTROSTATIC TRAP (METHOD I)

Our idea is to use the molecular complexity to our advantage. We show that, by using combined Zeeman and Stark effects, we can freely tune the slope ratio between two trapping potential surfaces and can increase the cooling efficiency. After we trap OH radicals in a static magnetic quadrupole trap, we superimpose an electrostatic quadrupole trap on top of the magnetic one. It is important that the electric and magnetic fields are parallel in the trapping region, which allows the calculation of total energy as a sum of Stark and Zeeman shifts. In Fig. 2(a), the contribution of the magnetic field to the energy levels is presented. The four Zeeman sublevels are easily recognizable. Let us analyze how these levels are affected by the presence of electric fields. We focus our attention on the low-field-seeking Stark levels from the f-doublet manifold that experiences a linear and positive Stark effect. In Fig. 2(b), the contribution presented is due to the electric field alone. Since all four levels are from the f doublet, all four states are low-field seekers (with respect to the electric field) with positive slopes only. In a combined magneto-electrostatic quadrupole trap, all four levels experience an additional positive energy shift. As a result, the slopes of the two sublevels [m₁ = 3/2, f] and [m₁ = 1/2, f] steepen, and the potential gradients of the two magnetically high-field seeking states [m₁ = −1/2, f] and [m₁ = −3/2, f] also rise with the increasing electric-field gradient. Whenever the contribution of the magnetic field is equal to that of the electric field, the combined potential gradient of these two states is zero. Therefore, at higher electric-field gradients, the molecules in the [m₁ = −1/2, f] state become confined in a very shallow potential well. The potential slope ratio between the [m₁ = 3/2, f] and the [m₁ = −1/2, f] states can be tuned to almost any value as a function of electric- and magnetic-field gradient ratios. For example, let us choose the magnetic and electric fields such that a ratio of 1/70 in potential slopes is formed. We define this ratio as $\varepsilon$.

The irreversible transition takes place near the classical turning point and changes the projection of the total angular momentum from 3/2 to −1/2, which reduces the total energy of a molecule 70- (1/ε) fold in a single step, eliminating the need for cycling. This irreversible transition can easily be performed by exciting the molecules on the Zeeman sensitive transition along the R₃ line of the A ²Σ₁/₂ (v = 0) ← X ²Π₁/₂ (v = 0) transition at 308 nm. We estimate that, at least, 11% (henceforth, referred to as $\gamma$) of the molecules will decay to the [m₁ = −1/2, f] state, given by the line intensities of the three possible branches, which are equal. Since the transition is Zeeman sensitive, the transition location can be chosen by tuning the wavelength to match the energy difference at a certain point. In the trap, these transition locations form a spherical shell where the excitations take place. Starting with the hottest molecules and slowly changing the transition frequency, lower energy molecules are accumulated in the shallow potential well, until the entire volume of the trap is swept.

Even though the focus region is relatively large, sufficient laser power for the scheme is readily available. By illuminating the trap with a beam intensity of $\sim 1$ W/cm², every molecule

![Image](https://via.placeholder.com/150)

FIG. 1. (Color online) Adiabatic energy levels of the OH radical in the ²Π₁/₂ electronic ground state in a magnetic quadrupole potential. In SPC, a molecule is excited around its classical turning point at the fully stretched m₁ = 3/2 and may decay to m₁ = 1/2 decreasing its energy threefold.
FIG. 2. (Color online) (a)–(c) Adiabatic energy levels of the OH radical in the $2\Sigma_{1/2}$ state in (a) a magnetic quadrupole, (b) an electric quadrupole, and (c) a combination of the two in which the field lines are parallel. All four potentials become traps in the combined quadrupole. The blue (upper solid) line corresponds to $|m_J = 3/2, f\rangle$ state, and the red (lower solid) line corresponds to the $|m_J = -1/2, f\rangle$ state.

that reaches the excitation shell has a probability of $\sim 1$ to scatter a photon [37]. The thicker the shell, which is determined by the bandwidth of the laser, the longer the period spent in it, the higher the scattering probability. This is a trade-off between the size of the shell and the laser power needed for the scheme since the residual translational energy grows with the shell size.

In a spherically symmetric trap, the spatial angular momentum and energy are conserved, which implies that the radius of the classical turning point (CTP) is constant. Since an excitation only removes translational energy in the radial direction, the molecules are left with residual translational energy in the angular direction. In the anisotropic case, the angular momentum is no longer conserved. If the angular momentum of a molecule varies quickly, compared to the time scale of the sweep process, then its CTP also changes rapidly. When the CTP moves up the potential barrier of the trap, energy conservation dictates that the residual angular velocity is lower. This means that the efficiency and density compression would only improve since SPC “catches” the molecules higher up the potential barrier of the trap due to the sweep order of the excitation process. Thus, modeling and simulating the process in a spherically symmetric potential, as opposed to an anisotropic potential, provides a lower limit for these values. Therefore, due to energy considerations, the estimated portion of molecules that can be trapped is $\epsilon$ [38], which corresponds to energy removal in one dimension. The resulting loading efficiency into the shallow trap is

$$\eta = \gamma \epsilon.$$  

We estimate that, for the case in which $1/\epsilon = 70$ and $\gamma = 11\%$, the loading efficiency would be greater than $10^{-3}$. We begin with a supersonic beam at $\sim 100$ mK. As we have shown, our moving magnetic trap decelerator conserves number density and temperature down to stopping velocities, so we expect to trap at least $10^6$ OH radicals in a $5 \times 5 \times 5$-mm$^3$ volume trap (a density of $\sim 10^{10}$ molecules/cm$^3$) in the fully stretched state [18] at the end of the deceleration process. Consequently, at the end of the SPC process, we will have $10^6$ molecules trapped in a $5 \times 5 \times 5$-mm$^3$ trap at a temperature of 2 mK. Now, as a final stage, the cold cloud can be adiabatically compressed (conserving the phase-space density) by increasing the electric-field gradient. The trap size can be reduced by a factor of $\sim 10^5$. The density of the trapped OH radicals will be $10^{12}$ molecules/cm$^3$ at the end of the process, 4 orders of magnitude higher than densities reported to date. At this density, the collision rate is about 1 kHz and should easily be observable. More generally, adiabatically resizing the trap compresses the molecule density as shown by the following equation:

$$C_\rho = \frac{\gamma \epsilon}{\epsilon^2} = \gamma \epsilon^{-2}.$$  

Monte Carlo simulations of this process were performed in order to verify the order of magnitude of the efficiency as well as the density compression predicted by this rough model. The results obtained in the simulations (Fig. 3) indeed verify the model.

In the simulations, a uniform distribution of molecules, both in velocity and in position, was randomly placed in the trap such that a constant number remained trapped inside. The trap potential used was linear in the radial direction as is formed by a magnetic quadrupole and perfectly spherically symmetric. The previous discussion has shown that such an isotropic potential would provide the minimal results in terms of efficiency and compression.

FIG. 3. (Color online) Monte Carlo simulations of Method I over 216 ms. The density compression and efficiency are plotted as a function of the trap depth ratio $\epsilon$. The simulations were performed with an initial uniform distribution in space and velocity, and $\gamma$ was taken as 11%. The results are in line with the orders of magnitude predicted by the model [Eqs. (1) and (2)].
The reason a uniform distribution is used is due to the
simplistic mathematical models developed, which uniformly
select parts of the distribution at different stages in the schemes.
These mathematical models are only designed to indicate the
order of magnitude of the physical properties of the scheme. In
fact, taking Gaussian initial distributions only further improved
the simulation results, although not by an order of magnitude,
which is easily understood since the trapped molecules have
lower energies than in the uniform case. Moreover, the uniform
distribution simplifies the model by making the ratio ε the only
physical aspect needed to describe the potentials.

The molecules were propagated in space-time via the
Runge-Kutta numerical approximation. The irreversible state
change was created via an instantaneous excitation to all
molecules in a region (replicating a saturated transition)
according to the scheme. Of them, 11% (γ) selected at random,
decay to state |m_f = −1/2, f⟩, retaining their position and
velocity, and the rest are removed from the simulation.

The excitation region was a spherical shell whose thickness
was 1/40 of the trap radius. All shells underwent the excitation
process sequentially from the outer portion of the trap to the
inner portion. Each shell was excited for a period of 3.6 ms for a
total of 144 ms for the entire excitation process. The molecules
were then propagated in the shallower well, whose slope was
determined by ε, without excitation for another 62 ms to allow
the over energetic ones to escape. This final period is important
to verify the number of trapped molecules.

The main advantage of this method is its efficiency, which
should be high enough to load molecules into a shallow optical
dipole trap to continue further cooling and compression of the
phase-space density (PSD). However, the main drawback of
this method is that it does not compress the PSD (as the PSD
stays constant during the adiabatic resizing of the trap) but can
only serve as a stepping stone to evaporative cooling, which
will compress the PSD. The second method does compress the
PSD as we show in the next section.

IV. SPC IN A MAGNETIC TRAP WITH AN
ELECTRIC-FIELD BARRIER (METHOD II)

In Method II, we again utilize both the Zeeman and the
Stark effects. We begin with a magnetic quadrupole trap such
that the energy levels of the OH radical in the 2Π_3/2 electronic
ground state are as illustrated in Fig. 1. Trap A is formed for
radicals in state |m_f = 3/2, f⟩ as shown in Fig. 4(a). Utilizing
the Stark effect, we add an electric-field gradient near the
classical turning point of the hottest molecules in trap A, which
can be seen by the perturbation in the energy levels for values
of Z above 3 mm displayed in Fig. 4(g). We will focus our
attention on the low-field-seeking Stark levels from the f-
doublet manifold. The electric-field gradient acts as a barrier
for molecules with parity f such that it blocks movement in the
Z direction and confines them in the transverse direction.

A possible implementation of such a barrier, as shown in
Fig. 4(b), is an electrostatic trap without the electrode that
closes the entrance. This configuration consists of two ring-
shaped electrodes with different radii and opposite potentials.
Both the low-field-seeking and high-field-seeking molecules,
with respect to the magnetic field, will see the electric-field
gradient as a barrier. For molecules in the |m_f = −1/2, f⟩
state, the electric-field gradient combines with the magnetic-
field gradient, which blocks the entrance, forming a shallower
and spatially smaller trap off-center from trap A. We will refer
to this trap as trap B.

The Stark and Zeeman adiabatic energy levels are simply
summed without regarding the angle between the electric and
the magnetic fields since the electric field is small enough
(<1 kV/cm). In this regime, both the Stark and the Zeeman
shifts are linear, and there are no level crossings [39]. (In
this scheme, only the states with total angular momentum
projections of 3/2 and −1/2 come into play.)

The molecules have a total angular momentum projection
of 3/2 in their initial state. A laser focused on the position

![Fig. 4. (Color online) (a) Shows the adiabatic energy levels required by Method II. Trap A for molecules with m_f = 3/2 is depicted by
the upper (blue) dotted line. Trap B for molecules with m_f = −1/2 is depicted by the lower (red) dotted line. (b) Shows a configuration of a
magnetic quadrupole formed by two current loops in an anti-Helmholz configuration and half an electrostatic trap formed by two ring-shaped
electrodes with potentials of opposite polarity, which create the potentials in (a). The electrodes confine the molecules in the transverse direction
such that trap B is formed. The dashed line energy levels in (a) do not participate in this scheme.

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of trap B (near the hottest molecules’ classical turning point) create the same electronic excitation described in Method I, which results in an estimated 11% (referred to as \( \gamma \)) of the molecules decaying to the \( |m_1 = -1/2, f \rangle \) state. In this state, the molecules are trapped inside trap B. A magnetic bias can now be gradually applied, moving the classical turning point of molecules with lower kinetic energy toward the loading point where they are also loaded into the trap. Alternatively, the barrier can be mechanically moved along the \( Z \) axis. The depth and size of trap B are determined by the height of the electric barrier and the gradient of the magnetic field.

In this case, the SPC does not take place over the entire volume of the large trap, but only a portion with a volume equal to that of trap B, differing from Method I. Defining the ratio of the radius of trap B to the radius of trap A as \( \chi \), we find that the instantaneous part of the spatial molecule distribution of trap A affected by SPC is \( \sim \chi^3 \). Taking into account the sweep of the entire \( Z \) coordinate via the tunable magnetic bias, at least \( \sim \chi^2 \) of the distribution is affected by SPC. This is the minimal portion since the molecule locations are dynamic, and therefore, the number of molecules that pass through the excitation volume grows in time. Therefore, the spatial portion, which lies between \( \sim \chi^2 \) and 1, grows with the time scale of the process.

We will now analyze the efficiency in terms of energy. We must take notice that, since the potential of trap A is spherically symmetric, this cooling scheme is one dimensional just like in Method I where this deduction was discussed in detail. Therefore, due to energy considerations, the portion of the molecules that can be trapped is \( \varepsilon \) [38], where \( \varepsilon \) is defined as the ratio of the energy depth of trap B to trap A. The resulting total minimum loading efficiency into trap B and minimal phase-space compression are as follows:

\[
\eta_{\text{min}} = \gamma \chi^2 \varepsilon, \quad (3)
\]

\[
C_{\text{min}} = \frac{\gamma \chi^2 \varepsilon}{\chi^3/2} = \gamma \chi^{-1} \varepsilon^{-1/2}. \quad (4)
\]

For the experimentally feasible ratios \( \varepsilon = 1/70 \) and \( \chi = 1/10 \), we find that \( C_{\text{min}} = 9.2 \), compressing the phase space by at least 1 order of magnitude. Monte Carlo simulations of this case show that, on a typical time scale of the process (108 ms), the resulting phase-space compression was greater than 2 orders of magnitude. This strengthens the prediction above that the time scale of the process can greatly enhance the performance with respect to the model discussed in Eqs. (3) and (4). The simulation results are provided in Fig. 5. Indeed, the same simulation over much shorter time scales displayed results closer to the minimal results predicted by the model verifying the hypothesis proposed, that the difference between the model and the simulation is a result of the time scale.

The description of the simulations is identical to the description provided in Method I except for the following differences. In this case, the uniform distribution makes the ratios \( \varepsilon \) and \( \chi \) the only physical aspects needed to describe the potentials. The region of excitation was a sphere with a radius determined by the proportion \( \chi \). Molecules that decay to state \( |m_1 = -1/2, f \rangle \) in the sphere were checked against the depth of the sphere, given by \( \varepsilon \), according to their kinetic energy, and the overenergetic ones were removed from the simulation. The sphere was moved continuously toward the center of trap A ending the process when its edge reached the center. The entire process was simulated over 108 ms.

Figure 5(a) shows that the phase-space density compression increases as \( \chi \) gets smaller. This effect is countered by the efficiency [Fig. 5(b)], which decreases as \( \chi \) gets smaller, lowering the total number of molecules trapped. Eventually, even though the compression increases, it becomes increasingly difficult to detect the resultant molecule samples, limiting the value of \( \chi \). The number of molecules in the sample at the beginning of the process along with the signal-to-noise ratios of the detection techniques will dictate this lower limit, and subsequently, the optimal choice of parameters.

**V. CONCLUSION**

The methods of implementation of SPC discussed and analyzed in this paper are very general and can be modified to cool almost any molecule that has an electric and magnetic dipole moment. Method I excels in efficiency, whereas, Method II excels in phase-space density compression. The time scales
spanned by these methods are 2 orders of magnitude lower than the total lifetime of the trap as opposed to any proposed cycling scheme. Both of these advantages make these methods excellent candidates as stepping stones for evaporative cooling and for creating dense molecular gases at any temperature between 100 and 1 mK. Experiments will most likely show that specific molecules will work better with one of the methods according to their traits (i.e., initial densities, length of process time scale possible, etc.). The robustness of these methods is a direct result of the lack of cycling. We plan to implement both of the methods and experimentally test the conclusions of this paper in the coming future.

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