

Sub-Doppler Cooling and Compressed Trapping of YO Molecules at μK Temperatures

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Complex molecular structure demands customized solutions to laser cooling by extending its general set of principles and practices. Compared with other laser-cooled molecules, yttrium monoxide (YO) exhibits a large electron-nucleus interaction, resulting in a dominant hyperfine interaction over the electron spin-rotation coupling. The YO ground state is thus comprised of two manifolds of closely spaced states, with one of them possessing a negligible Landé g factor. This unique energy level structure favors dual-frequency dc magneto-optical trapping (MOT) and gray molasses cooling (GMC). We report exceptionally robust cooling of YO at $4\ \mu\text{K}$ over a wide range of laser intensity, detunings (one- and two-photon), and magnetic field. The magnetic insensitivity enables the spatial compression of the molecular cloud by alternating GMC and MOT under the continuous operation of the quadrupole magnetic field. A combination of these techniques produces a laser-cooled molecular sample with the highest phase space density in free space.

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I. INTRODUCTION

Ultracold molecules [1,2] offer a new platform for quantum chemistry [3–5], strongly correlated quantum systems [6], quantum information processing [7–13], and precision tests of fundamental physics [14–22]. There has been a long quest to create dense samples of ultracold molecules. Various molecular slowing methods have been proposed [23–25] and demonstrated [26–32]. Optoelectrical Sisyphus cooling has created polar molecular samples with submillikelvin temperatures [33]. Ultracold diatomic molecules have been synthesized from ultracold atoms [34–39], and, very recently, a quantum degenerate gas of alkali molecules has been realized [40]. Elastic atom-molecule interactions provide thermalization [41] and collisional cooling [42]. Molecular ions have also been sympathetically cooled with cotrapped atomic ions, and quantum logic spectroscopy [43–45] has been successfully implemented [46–48].

Direct laser cooling of molecules provides a potentially species-independent approach for producing cold molecules. However, extending techniques used for laser

cooling of atoms to molecules is challenged by the absence of cycling transitions associated with the complexity of molecular structure. To remove the large number of dark states in the form of rovibrational levels so that sufficient photon scatterings are ensured, cooling transitions should have maximally diagonal Franck-Condon factors [49] and optimized angular momentum selection rules [50]. Following these initial proposals, the past few years have witnessed a rapid progress of laser cooling and trapping of molecules. Magneto-optical traps of diatomic molecules have been demonstrated for SrF [51], CaF [52,53], and YO [54,55]. Sisyphus-type cooling was reported using gray molasses cooling (GMC) for CaF and SrF to $50\ \mu\text{K}$ [52,56,57] and using magnetically assisted laser cooling for YbF to $100\ \mu\text{K}$ [58]. Triatomic molecules of SrOH and YbOH were cooled to approximately $600\ \mu\text{K}$ in one dimension [59,60]. GMC has been further enhanced with velocity-selective coherent population trapping, enabling deep cooling of CaF to $5\ \mu\text{K}$ [61,62]. Consequently, loading of molecules into optical dipole traps [56], magnetic traps [57,63], and optical tweezer arrays [64] has also been achieved. Other molecules that are currently under active investigations for direct laser cooling include BaH [65], MgF [66], BaF [67,68], AlF [69], and CH [70].

In this work, we employ an effective cooling and trapping protocol that is specifically tailored for the unique structure of $^{89}\text{Y}^{16}\text{O}$ molecules. The techniques we develop to address the specific challenges and opportunities for YO can also be applied to a class of molecules that share a similar energy level structure. The presence of two

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independent electron-nuclear spin angular momentum states in the molecular ground state provides two quasi-independent paths for efficient GMC, along with robust dual-frequency dc magneto-optical trapping (MOT). The GMC-based approach provides the lowest laser-cooled molecular temperature of $4 \mu\text{K}$ over a broad range of laser tuning and magnetic field (B), such that exciting a Raman resonance does not bring further cooling, in contrast to previous reports [61,71–77]. GMC is known to be magnetic field insensitive [78–80], and this insensitivity is further enhanced in YO molecules by the existence of a ground state manifold with a negligible Landé g factor. This feature enables the GMC to perform exceptionally well even at $B = 25 \text{ G}$, which is typically regarded as too large for sub-Doppler cooling to work [78,81]. Additionally, magnetically induced Sisyphus cooling [58,59,82–84] is observed under this field. This robust cooling mechanism against large B allows us to demonstrate a novel scheme to significantly compress the molecular cloud by combining dc MOT trapping and sub-Doppler cooling.

II. YO STRUCTURE

The ground state $X^2\Sigma^+$ of YO belongs to Hund's case (b) [85]. The single valence electron resides mostly in the s orbital of the yttrium atom [86], and its wave function has a strong overlap with the yttrium nucleus. As a result, the electron spin $\mathbf{S} = 1/2$ and the yttrium nuclear spin $\mathbf{I} = 1/2$ are coupled strongly by the Fermi contact term in the hyperfine interaction, forming an intermediate $\mathbf{G} = \mathbf{S} + \mathbf{I}$. This is further coupled with molecular rotation \mathbf{N} by an electron spin-rotation interaction to form $\mathbf{F} = \mathbf{G} + \mathbf{N}$. The excited state $A^2\Pi_{1/2}$ follows a typical Hund's case (a). The total angular momentum can be written as $\mathbf{F}' = \mathbf{J}' + \mathbf{I}$, where \mathbf{J}' is the total angular momentum excluding \mathbf{I} . The cooling transition employs $X^2\Sigma^+(N=1) \rightarrow A^2\Pi_{1/2}(J'=1/2)$ [54,55,87] to minimize the number of lasers required to create a quasicycling transition [50]. The complete repumping scheme is described in Supplemental Material [88].

For $X^2\Sigma^+$, a considerable magnetic moment comes only from the electron spin. For the $G=0, F=1$ manifold, the Landé g factor is 0.01 in the weak field limit, where B is not sufficiently strong (hundreds of G) to decouple the electron spin from the nuclear spin [89].

III. DC MOT

Our systematic investigation of sub-Doppler cooling of YO begins with a dc MOT [90,91] loaded with the buffer-gas-cooled and laser-slowed YO molecules [55,87,88]. Depending on the hyperfine states, shown in Fig. 1(a), the optimal laser frequency detunings and polarization settings vary accordingly to provide robust trapping forces arising from a dual-frequency MOT [90], a red-detuned type-I ($F' > F$) MOT, or a red-detuned type-II ($F' \leq F$) MOT [91].

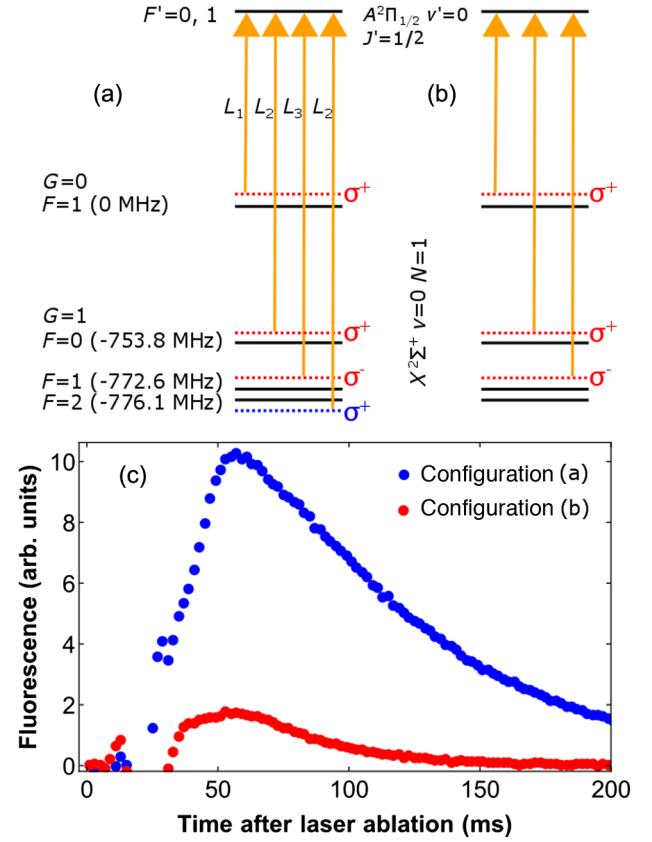


FIG. 1. The dc MOT. (a) The optimal polarization settings for all the hyperfine components for the dual-frequency MOT. For illustration purposes, we show the polarization of the beam propagating along the $-z$ direction, and the magnetic field points along $+z$ at positions $z > 0$ [90,92]. The hyperfine structure of the excited manifold is not resolved. (b) The optimal polarization settings for the red-detuned MOT. (c) Differential MOT fluorescence between two opposite quadrupole field directions, for the laser configurations shown in (a) and (b). We switch on a magnetic field gradient of 12 G/cm at 23 ms , and the loading process takes about 35 ms .

Considering its robust performance, we start our discussion with the dual-frequency MOT. To generate the laser beams, we split the main cooling laser into three beams. Beam L_1 (L_3) is red detuned from $G=0, F=1$ ($G=1, F=1$), and beam L_2 contains two optical fields red detuned from $G=1, F=0$ and blue detuned from $G=1, F=2$. For more details, see Supplemental Material [88].

The dual-frequency MOT lifetime decreases with the increasing MOT beam intensity, which suggests a loss mechanism of optical pumping to dark states. We set a nominal intensity $I = 1.4I_0$ for the dc MOT, where $I_0 = 2.7 \text{ mW/cm}^2$ is the estimated saturation intensity. At this intensity, the detunings for the hyperfine components, from top to bottom in Fig. 1(a), are tuned to be $-5.8, -9, -5.8,$ and $+2.6 \text{ MHz}$, respectively, to maximize the number of trapped molecules, resulting in a MOT lifetime of 90 ms .

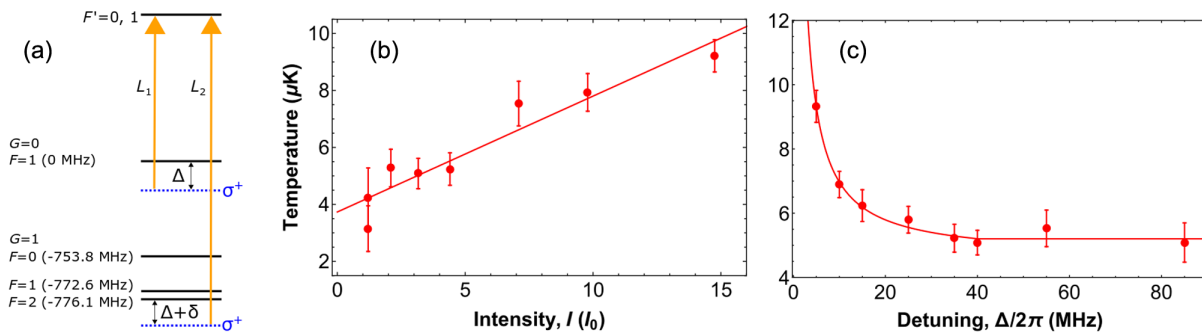


FIG. 2. Characterization of GMC. (a) Configuration of laser detunings. (b) Temperature versus intensity I with single-photon detuning $\Delta = 8.3\Gamma$ and Raman detuning $\delta = 0$ between the $G = 0$, $F = 1$ and the $G = 1$, $F = 2$ manifolds. The solid line is a linear fit. (c) Temperature versus Δ with $I = 3.2I_0$ and $\delta = 0$. The solid line is a fit to the function $T_{\text{avr}} = 1/\Delta + T_0$, where T_0 represents a background temperature. The error bars in the plots correspond to 1σ statistical uncertainty, and the fittings are consistent with the theoretical predictions in Ref. [78].

The molecular sample has a 2σ diameter of 2.8 mm (3.9 mm) along the axial (radial) direction and a temperature of 2 mK. The number of trapped molecules is 1.1×10^5 , 7 times that reported in our previous work of the rf MOT [55]. This increase comes from the dual-frequency MOT mechanism and a number of technical optimizations involving the trapping and repumping lasers, the buffer-gas cell, and the vacuum.

The dual-frequency MOT has contributions from the other two trapping mechanisms, red-detuned type-I and red-detuned type-II MOT [90,91]. To determine their relative contributions, we disable the blue-detuned component in L_2 , shown in Fig. 1(b), and study the consequences on the MOT performance. As shown in Fig. 1(c), without the blue component the MOT produces 5 times fewer molecules and half of the lifetime as compared with the dual-frequency MOT. This feature clearly demonstrates that the dual-frequency trapping mechanism dominates the trapping force for the MOT [90].

The YO dual-frequency MOT further benefits from the close spacing (3.5 MHz) of $G = 1$, $F = 1$ and $G = 1$, $F = 2$, in comparison to the cooling transition linewidth of $\Gamma = 2\pi \times 4.8$ MHz [93]. Therefore, $G = 1$, $F = 1$ and $G = 1$, $F = 2$ both contribute to the dual-frequency trapping mechanism, increasing the overall trapping efficiency. This feature may be responsible for our observation that the dc MOT traps approximately 20% more molecules than the rf MOT [55] given that the other conditions are the same, contrary to the results reported for CaF [53] and SrF [94].

It is experimentally found that the red-detuned MOT [Fig. 1(b)] already employs the correct polarization for both laser components addressing the $G = 1$ manifold. For the two closely spaced states of $G = 1$, $F = 1, 2$, the corresponding laser polarization produces trapping for $G = 1$, $F = 2$ and antitrapping for $G = 1$, $F = 1$ [91], which shows that the force from $G = 1$, $F = 2$ overwhelms that from $G = 1$, $F = 1$, consistent with the observation in Ref. [92] for SrF molecules.

IV. GRAY MOLASSES COOLING

Once the dc MOT is loaded, we blue detune L_1 , remove the red-detuned component of L_2 , and switch off L_3 and the quadrupole magnetic field for gray molasses cooling [78,95,96]. GMC works on type-II transitions and relies on position-dependent dark states that are formed from the spatial variation of the laser polarization and intensity. Molecules optically pumped into dark states can come out to a bright state via motion-induced nonadiabatic transitions [95]. On average, the spatially varying ac Stark shift of the bright state gives rise to motional damping more often than acceleration, leading to Sisyphus-type cooling [95].

Unlike the hyperfine structure of SrF and CaF, YO has a large frequency gap between $G = 0$ and $G = 1$, shown in Fig. 2(a). As a result, the two laser components L_1 and L_2 independently address these two manifolds, unless they are tuned close to a Raman resonance ($\delta = 0$). After 8 ms of GMC, we determine the temperature of the molecular cloud using standard ballistic expansion measurements. For a wide range of parameters that we explore in this work, the molecular temperature remains robustly below 10 μK [Figs. 2(b) and 2(c)]. To make an accurate measurement of such low temperatures, we compress and cool the cloud first using a novel scheme, described in detail below. Unless otherwise specified, we plot the average temperature $T_{\text{avr}} = T_r^{2/3} \times T_a^{1/3}$, where T_r and T_a are the temperatures along the radial and axial directions, respectively.

The YO temperature depends on the molasses beam intensity and frequency detuning in a way consistent with theory [78]. As shown in Figs. 2(b) and 2(c) for $\delta = 0$, the temperature increases linearly with the intensity and decreases with the detuning before settling down to a constant. Similar detuning dependence has been reported in other systems [62,76,77,96]. The momentum diffusion coefficient D_p increases (decreases) with intensity (detuning), while the damping coefficient α is both intensity and

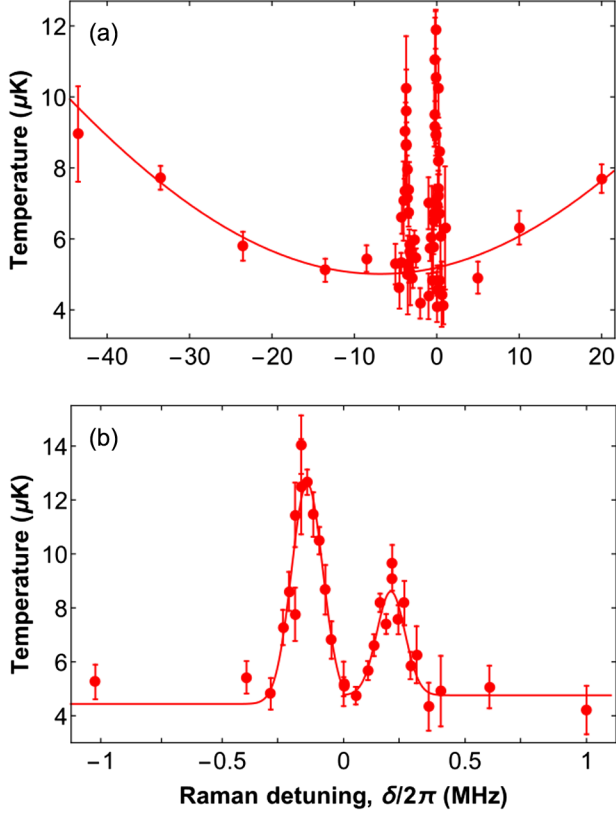


FIG. 3. Scan of δ in GMC. (a) Temperature versus δ , with $I = 3.2I_0$ and single-photon detuning $\Delta = 8.3\Gamma$ for $G = 0, F = 1$. The temperature is elevated near two Raman resonance conditions $\delta = 0$ (for $G = 1, F = 2$) and $\delta/2\pi = -3.5$ MHz (for $G = 1, F = 1$). The solid line is a guide for the eye. (b) Enlarged scan near the resonance condition $\delta = 0$, with $I = 3.2I_0$ and $\Delta = 12.5\Gamma$. The solid lines are Gaussian fits.

detuning insensitive [78]. The temperature is determined by $k_B T = D_p/\alpha$, where k_B is the Boltzmann constant. The fittings in Figs. 2(b) and 2(c) are consistent with this model. It is worth mentioning that, for an intensity smaller than the minimum value shown in Fig. 2(b), the molasses becomes too weak to hold molecules against gravity.

This behavior is similar to the sub-Doppler cooling with type-I transitions [97], where $T \propto |\Omega|^2/\Delta$. Here, Δ is the detuning and Ω is the Rabi frequency, which is proportional to \sqrt{I} .

To understand the performance of GMC around a Raman resonance, we next investigate the temperature dependence on the Raman detuning δ while keeping $I = 3.2I_0$ and the single-photon detuning $\Delta/2\pi$ for $G = 0, F = 1$ fixed at +40 MHz ($8.3\Gamma/2\pi$). The cooling is insensitive to δ over an extensive range, as shown in Fig. 3(a). For $\delta/2\pi = -43.5$ MHz, the remaining component of L_2 is on resonance with $G = 1, F = 1$. Thus, cooling (to $9 \mu\text{K}$) arises purely from the $G = 0, F = 1$ manifold. Similarly, if we set L_1 on resonance with $G = 0$ while having L_2 blue detuned from $G = 1$, the cooling temperature reaches as low as

$15 \mu\text{K}$. We thus conclude that both the $G = 0$ and the $G = 1$ manifolds are responsible for GMC, and their combination leads to efficient sub-Doppler cooling of molecules to the lowest temperature while being robust against the Raman detuning [98].

When δ is tuned slightly away from 0, we observe striking rises of temperature, followed with quick decreases back down to $4 \mu\text{K}$ when $|\delta|$ becomes sufficiently large of a few hundred kilohertz. The two resonancelike features are symmetrically located around $\delta = 0$ as shown in Fig. 3(b). Reference [61] reports a similar rise of temperature away from $\delta = 0$ for CaF. For YO, beyond the two peaks, the temperature returns quickly to the same value as that on the Raman resonance. The observed peak width and splitting between the two temperature peaks increase (decrease) with the laser intensity (the single-photon detuning Δ). Our understanding for this effect is the following. GMC depends on transient dark states [78,80], and, generally, a less stable dark state causes more momentum diffusion and leads to a higher temperature. Near the Raman resonance condition, dark states formed in both $G = 0, F = 1$ and $G = 1, F = 2$ can be destabilized by their cross-coupling. It leads to enhanced photon scattering and deteriorated cooling over a range on the order of the two-photon Rabi frequency Ω_R . This result is different from the $\delta = 0$ situation, where a new stable dark state is formed with the superposition of Zeeman sublevels from different hyperfine states [61,62], resulting in a Λ -type GMC.

A similar temperature increase is observed for the applied microwave coupling between the $N = 0$ and the $N = 1$ states that is used to create a quasicycling transition (see Supplemental Material [88]), where the achieved temperature is always $>15 \mu\text{K}$. We thus switch off the microwaves for state remixing during GMC. Note that the approximately 15% of molecules initially populated in $N = 0$ states are lost.

V. GMC UNDER B

Considering the negligibly small Landé g factor for $G = 0$, it is interesting to explore how well GMC performs in the presence of B . We apply a magnetic field along the axial direction and measure the temperatures both along and perpendicular to B with $\delta = 0$. Figure 4 demonstrates that the GMC is surprisingly robust over a large range of B values, along with a few remarkable features.

First, the temperature appears to have a pronounced peak near 0.3 G. This resonancelike feature is attributed to the Zeeman shifts of the $G = 1, F = 2$ sublevels that destabilize the dark state formed both in its own manifold through Larmor precession and in the $G = 0, F = 1$ manifold through Raman coupling. The temperature dependence on B then becomes flat between 0.6 and 4 G, regardless of whether L_2 is tuned on resonance with $G = 1, F = 2$ or remains on Raman resonance with L_1 .

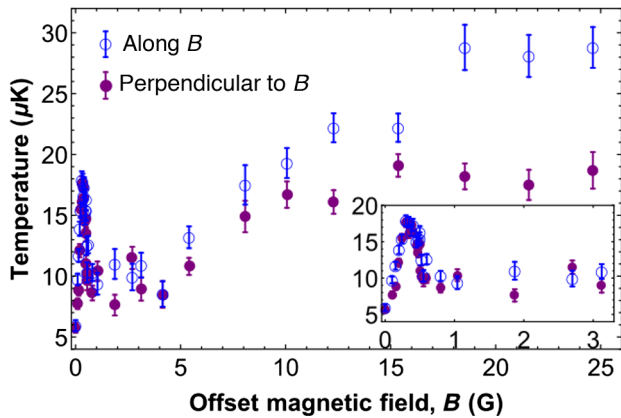


FIG. 4. Temperature under a uniform B applied along z , with $I = 3.2I_0$, $\Delta = 8.3\Gamma$, and $\delta = 0$. The blue open circles (purple filled points) represent the temperature measured along (transverse to) B . The inset shows the temperature from 0 to 3 G.

This observation reveals that, within this range of B , GMC arises mostly from $G = 0$, $F = 1$, which has a small Landé g factor and, thus, forms a relatively stable dark state.

At approximately 4 G, the temperature starts to rise with B , indicating that the dark state in $G = 0$, $F = 1$ becomes unstable. The temperature measured in the direction perpendicular to B rises slower than that along B and reaches a plateau after approximately 10 G. This effect is attributed to the magnetically induced Sisyphus cooling [58,59,82–84], after the original GMC becomes less effective. The laser field pumps YO into a dark state, which is remixed with a bright state via Larmor precession. This process damps the molecular motion in a Sisyphus fashion [83]. In the direction transverse to B , the spatially varying dark and bright state mixing is much stronger than that along B , resulting in lower temperatures. The magnetically induced Sisyphus cooling works at approximately 25 G for YO, substantially larger than any other atoms or molecules [58,59,82–84], where the field applied is nominally approximately 1 G. Again, such an exceptional magnetic insensitivity must be attributed to the small Landé g factor of $G = 0$, $F = 1$.

VI. COMPRESSION

Such exceptionally robust GMC against the magnetic field brings an intriguing capability. In the presence of the quadrupole magnetic field used for the MOT, molecules can still be cooled via GMC to a temperature much lower than that for the MOT. Thus, with the quadrupole field turned on continuously, we can alternate the laser beams between MOT and GMC parameters so as to apply the strong trapping force of the MOT to the ultralow-temperature molecular sample prepared by GMC. This scheme works effectively, as the GMC process is fast relative to MOT heating, such that the compression from the MOT dominates over the expansion during the GMC.

We measure the cooling (heating) speed of GMC (MOT) by recording the temperature for different GMC (MOT) pulse durations, as shown in Figs. 5(a) and 5(b). The cooling speed ($1/\tau$) increases with the laser intensity and is not sensitive to the detuning between 1Γ and 6.2Γ . With the full laser power ($30I_0$) and detuning 3.1Γ , molecules are cooled from 2 mK to $100\ \mu\text{K}$ with a $1/e$ time constant $\tau \sim 94\ \mu\text{s}$. The MOT heating process, on the other hand, takes approximately 1 ms.

We first ramp the magnetic field gradient of the dc MOT from 12 to 47 G/cm in 5 ms and hold at this value for another 5 ms for initial compression [99,100]. The MOT stabilizes with a diameter of 1.4 mm (2.4 mm) along the axial (radial) direction. We then apply a 2 ms GMC pulse to cool the molecules followed by another MOT pulse with a varying duration for compression. The cloud size is measured right after the MOT pulse, as shown in Fig. 5(c). The cloud size shrinks until approximately 4 ms and is significantly smaller than the equilibrium MOT size. This compression process is dynamical, and the cloud eventually reaches the original MOT size [Fig. 5(c)].

For our optimized compression sequence, we repeat the GMC-MOT cycle 3 times in 10 ms after the initial 5 ms MOT hold pulse (see Supplemental Material [88]). We do not observe considerable molecule loss during the compression except those optically pumped into the unaddressed dark states. After the compression, the cloud has a

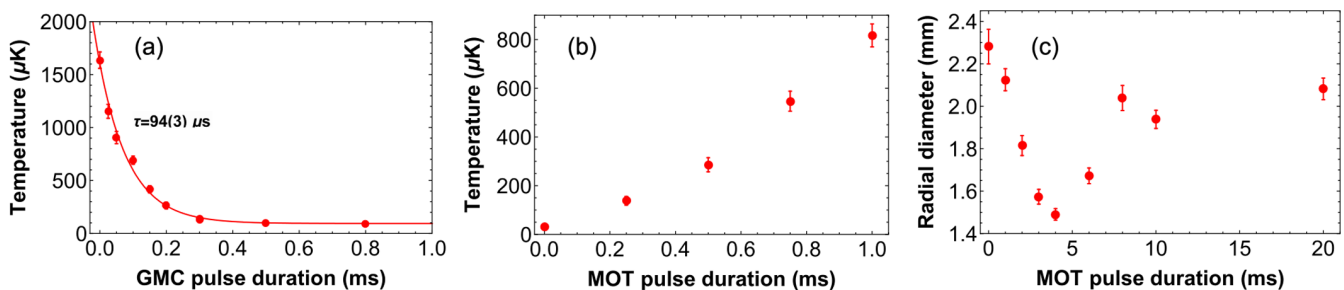


FIG. 5. Compression of the molecular cloud by combining the GMC with the dual-frequency dc MOT at a B gradient of 47 G/cm. (a) Temperature versus the duration of the GMC pulse, with $I = 30I_0$, $\Delta = 3.1\Gamma$, and $\delta = 0$. The solid line is an exponential fit. (b),(c) Temperature and *in situ* diameter of the molecular cloud versus the duration of a single MOT pulse, which is applied after the 2 ms GMC pulse.

diameter of 0.69 mm (0.93 mm) along the axial (radial) direction. The corresponding volume is approximately 10 times smaller than that before the compression, with approximately 5×10^4 molecules remaining and a peak spatial density of $5.4 \times 10^7 \text{ cm}^{-3}$. The molecules are then cooled to 4 μK with a final 8 ms GMC pulse, creating a molecular sample with a peak phase space density of 3.3×10^{-8} . Both the spatial density and the phase space density are higher than the previous best values in free space [61].

VII. CONCLUSION

We have investigated a wide range of cooling and trapping strategies based on the particular energy level structure of YO molecules, demonstrating both red-detuned and dual-frequency dc MOTs along with robust, field-insensitive sub-Doppler cooling to 4 μK with gray molasses cooling. We explored the relation of Raman resonance and GMC, clarified the role of a Λ -type system in GMC, and demonstrated magnetically induced Sisyphus cooling. In addition, we invented a novel scheme to compress the molecular cloud by combining the MOT spring force with the magnetic-insensitive GMC, which improves the phase space density by one order of magnitude. This compression scheme may be applicable to a variety of molecules and atoms. Given the insensitivity of GMC to laser detuning (both one photon and two photon), the compressed ultracold molecular cloud can be readily loaded into an optical dipole trap with high efficiency in the presence of cooling, paving the way for study of ultracold molecular collisions and chemistry, investigation of dipolar quantum gases, and quantum simulation of many-body systems. It is also feasible to load the molecules into an array of optical tweezers [64] for quantum information processing [7–10,101]. The demonstrated techniques address strong Fermi contact interaction, which is relevant for molecule-based precision measurement such as the search for parity-violating nuclear anapole moments [16,22].

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