Polarization Enhanced Deep Optical Dipole Trapping of Λ-cooled Polar Molecules

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We demonstrate loading of SrF molecules into an optical dipole trap (ODT) via in-trap Λ-cooling. We find that this cooling can be optimized by a proper choice of relative ODT and Λ beam polarizations. In this optimized configuration, we observe molecules with temperatures as low as 14(1) µK in traps with depths up to 570 µK. With optimized parameters, we transfer ~5% of molecules from our radio-frequency magneto-optical trap into the ODT, at a density of ~2 × 10^9 cm^-3, a phase space density of ~2 × 10^-7, and with a trap lifetime of ~1 s.

Ultracold molecular gases can be produced either by assembly from ultracold atoms [1–5], recently leading to the first demonstration of a quantum degenerate molecular gas [6], or by direct cooling and trapping of molecules. Recent progress on the latter path includes demonstrations of magneto-optical trapping (MOT) [7–10], sub-Doppler cooling [11, 12], loading into conservative magnetic quadrupole [13, 14] and optical dipole traps (ODTs) [15, 16], and observation of molecules—molecule [17–19] and molecule-atom [20] collisions. These improvements on both paths to cold molecules bring us closer to realizing their potential as platforms for quantum simulation [21–24], quantum information [25, 26], and precision measurement [27–29].

These applications all require molecular gases with high density and low entropy, i.e., in or near the regime of quantum degeneracy. Achieving this in directly cooled molecular species will likely require evaporative cooling, either of atoms that are co-loaded with molecules in a sympathetic cooling approach [30–32] or by using just the molecular species [33]. This requires achieving high enough density that rethermalizing collisions occur rapidly. Increasing the initial phase-space density is also desirable, as starting closer to unity will minimize the loss of molecules during collisional cooling.

In this Letter, we demonstrate the ability to reduce the temperature, T, (and thus maximize density, n, and phase space density Φ) within an ODT of strontium monofluoride (SrF) by determining optimal polarizations of both the cooling and trapping light. We have produced gases of up to N_{ODT}~160 trapped molecules with T~14 µK, n~2 × 10^9 cm^-3, and Φ~2 × 10^-7.

Our apparatus is illustrated in Fig. 1(a). SrF molecules from a cryogenic buffer gas beam source [34] are slowed [35], then cooled and trapped in an rfMOT [8, 36] (N_{MOT}~3500 molecules, T_{MOT}~1 mK, Gaussian width σ_{MOT}~1 mm). The rfMOT requires laser frequencies addressing all four |X^2Σ^+, v = 0, N = 1, J, F⟩ hyperfine levels (Fig. 1(b)), coupling them to the |A^2Π_{1/2}, v' = 0, N' = 0, J' = 1/2, F'⟩ state, along with repumpers for the X(v = 1, 2, 3) vibrational states. To use laser power efficiently, a single beam containing all needed frequencies is cycled through all three orthogonal axes of the rf-MOT, then retro-reflected, to provide trapping and cooling along all axes. To compensate for power loss due to optical elements along the path, an adjustable Keplerian telescope is used to control the convergence of the MOT beams.

Efficiently loading an ODT typically requires temperatures of < 0.1/10 the trap depth [37], which is at most 570 µK in our apparatus. Ideally, the cooling method should be effective both inside and outside the trap volume. One technique demonstrated to reach the required temperature in similar molecules (CaF and YO) requires coupling two hyperfine levels in the |X^2Σ^+, N = 1⟩ manifold to |A^2Π_{1/2}, J = 1/2⟩, with an overall blue detuning ∆ and a relative Raman detuning δ (Fig. 1(b)), to create a Λ system [12, 15]. This ‘Λ-cooling’ approach combines gray molasses [11] with the velocity-selective coherent population trapping (VSCPT) characteristic of Λ systems [38, 39], and is commonly used for loading alkali atoms into optical dipole traps [40]. In CaF, coupling the |F = 2, J = 3/2⟩ and |F = 1, J = 1/2⟩ levels was found to cool molecules to T~0.1 µK in free space [15].

However, although SrF has a very similar level structure to CaF, we find that coupling the analogous pair of states in SrF does not result in effective cooling. Instead, we observe cooling to T~10 µK in free space when coupling the |F = 1, J = 3/2⟩ and |F = 1, J = 1/2⟩ states for ∆/(2π) > 9 MHz = 1.4Γ (where Γ/(2π) = 6.63 MHz is the natural linewidth of the X → A transition). So, in all the work described here we use those states for Λ-cooling (Fig. 1(b)). This dependence on which state is coupled to |F = 1, J = 1/2⟩ is also evident in a numerical simulation based on solving the Optical Bloch Equations (OBEs) [41]. For SrF, the simulation shows a much stronger damping force when using |F = 1, J = 3/2⟩ than when using |F = 2, J = 3/2⟩.

In CaF, Λ-cooling was also shown to be effective within the ODT [15]. This is remarkable, since—unlike alkali atoms in the |^3S_{1/2}⟩ ground state—molecules in a ^2Σ^+, N = 1 state have substantial vector and tensor polarizabilities even for far-detuned traps [42], which lead to differential shifts between the substates of each hyper-
The ODT, formed by focusing a ~50 W single-mode
1064 nm laser beam to a 1/e²-radius of ~40 µm, is turned
on at the same time as the Λ-cooling. This laser is
combined with one Λ-cooling beam pass using a dichroic
mirror, then passes through a λ/4 plate before entering the
chamber. We have measured the Jones matrix of those
elements, which, along with the orientations of additional
λ/2 and λ/4 waveplates (lower-left, Fig. 1(a)) in the ODT
beam path prior to the dichroic, determines the polarization
of the trap light.

The trap depth for a given ODT intensity is deter-
mained by calculating the AC Stark shift based on mea-
sured [45, 46] and/or calculated [47, 48] dipole matrix
elements between the |X²Σ⟩ ground state and all ex-
cited states [49]. Then, by measuring the beam pro-
file along the ODT axis (z), we determine the full axial
trap depth profile TD(z) (Fig. 1(c)) and maximum trap
depth TD,0 = 570 µK. The profile deviates from the ideal
quadratic behavior due to astigmatism of the ODT beam.

After 150 ms of simultaneous application of ODT and
Λ beams, the Λ-cooling light is shuttered for a time tsh
(50 ms unless otherwise indicated), to allow untrapped
molecules to fall from the imaging region. Then, Λ-
cooling light is turned back on for 150 ms, during which
the camera is exposed. Trapped molecules remain cold
because the Λ-cooling is effective inside the trap. The peak trap-
induced scalar AC stark shift for the X state (A state)
is -11.9 MHz (+0.4 MHz) under our conditions. These
turns to redshift the one photon detuning in the trap
result in an in-situ image of optically trapped molecules. Our imaging system does not resolve
the width of the cloud along the radial dimension of the ODT
dimension (z). However, the width of the molecular cloud
along the horizontal axis (Σ) is large enough to be resolved by our camera, whose hori-
zonal axis is at 45° with respect to the ODT axis (ẑ). The cloud density profile along the ODT axis, n(ẑ), is de-
termined by integrating the image along y (Fig. 2(a-c)). With knowledge of both T_{D}(ẑ) and σ_{ax}, the tempera-
ture T can be determined from n(ẑ). We also measured T
through time-of-flight (TOF) expansion and found re-
sults consistent with, albeit less precise than, the tem-
peratures measured from the in-situ axial distribution.

We expected that cooling inside the trap would be sensi-
tive to the polarization of the trap laser, due to the differ-
ential AC Stark shifts [42, 50–52] in the |X²Σ⟩ state.
The largest of these shifts within the two coupled hyper-
fine manifolds are ~10% of the scalar (i.e., average) AC
stark shift (Fig. 2(f)). We anticipated that the optimum
polarpizations would be those for which two states, one
within each of the |1, 3/2⟩ and |1, 1/2⟩ manifolds, expe-
rience the same AC stark shift (Fig. 2(f)) and thus form
a coherent dark state both inside and outside the trap.
Since there is no other applied field to define a quantiza-
In an attempt to understand this unanticipated dependence, we expected the cooling to depend only on the aspect ratio of the ODT light polarization ellipse, and not on its orientation or rotation direction.

Instead, we found that the cooling can strongly depend on the direction of rotation of the polarization of the ODT beam. To quantify this dependence, we define the ellipticity, $\gamma_{ODT}$, in terms of the dimensionless Stokes parameters ($S_{1,2,3}$) of the trap light [53]. Specifically, $\gamma_{ODT} = \frac{1}{2} \tan^{-1} \frac{S_1}{\sqrt{S_1^2 + S_2^2}}$. The sign of $\gamma_{ODT}$ indicates the direction of rotation of the electric field vector (when viewing along the direction of light propagation), with $\gamma_{ODT} > 0$ indicating clockwise, while $\tan(\gamma_{ODT})$ is the ratio of minor to major axes of the polarization ellipse.

We found that the symmetry between positive and negative $\gamma_{ODT}$ is broken by an intensity imbalance between the counter-propagating $\Lambda$-cooling beams, which have opposite circular polarizations. Such an intensity imbalance can arise easily in our apparatus, where the $\Lambda$-cooling beam co-(counter)-propagating to the ODT beam is the last (first) pass of the long path of the retro-reflected $\Lambda$-cooling beam through the trapping chamber (Fig. 1(a)). For example, if the $\Lambda$-cooling beam is collimated then, due to losses through optical elements on the path, the final pass has only 74% of the first pass intensity. The ratio of intensities of final to first pass, $R_{IA}$, can be increased (decreased) by making the beam mildly convergent (divergent).

Data showing the effect of this broken symmetry on the in-trap molecule temperature is shown in Fig. 2. Fig. 2(a) shows the results for a collimated beam ($R_{IA} = 0.74$) when the $\Lambda$ beam co-propagating with the ODT is $\sigma^+$ polarized while the counter-propagating beam is $\sigma^-$ polarized. We find that the molecular cloud width, and thus the in-trap molecule temperature is shown in Fig. 2. Fig. 2(a) shows the results for a collimated beam ($R_{IA} = 0.74$) when the $\Lambda$ beam co-propagating with the ODT is $\sigma^+$ polarized while the counter-propagating beam is $\sigma^-$ polarized. We find that the molecular cloud width, and thus the in-trap molecule temperature is shown in Fig. 2(a).

In an attempt to understand this unanticipated depen-
of \( T \) on \( \gamma_{ODT} \), we developed an OBE solver [41] with the capability to include intensity imbalanced, retro-reflected beams. We explicitly add the AC Stark Hamiltonian from the ODT light (including vector and tensor shifts), while AC Stark shifts from the imbalanced \( \Lambda \) beams (which can be of comparable magnitude to those from the ODT laser under our conditions [49]) are included implicitly in the OBEs. This solver was benchmarked using results from comparable solvers [41, 54] and also against experimental observations, such as rMOT trap temperature [8] and capture velocity, \( \Lambda \)-cooling [15], and single frequency cooling [44]. However, we were not able to reproduce the effects shown in Fig. 2. So, the mechanism behind the observed interplay between ODT polarization and \( \Lambda \)-beam intensity imbalance remains an open question.

We next worked to optimize \( \delta \) and \( R_{1↑,1↓} \). In Fig. 3(a), we observe that \( T \) is optimized near two-photon resonance (\( \delta = 0 \)) with a broad minimum extending to \( \delta > 0 \). Similar behavior has been observed in other \( \Lambda \) cooling experiments [15, 38, 55]. The breadth of this feature is comparable to the in-trap two photon Rabi frequency between the coupled hyperfine manifolds (\( \Omega_{A}/(2\pi) \approx 8 \text{ MHz} \) [49]), as expected. We also observe that \( T \) is optimized for a hyperfine intensity ratio \( R_{1↑,1↓} \approx 2/3 \) (Fig 3(b)), and becomes inefficient for \( R_{1↑,1↓} \lesssim 0.25 \). We note in particular that ‘single frequency cooling’ (where \( R_{1↑,1↓} = 0 \)—which was shown to lead to \( T < 10 \mu \text{K} \) in free space for CaF [44]—is ineffective at cooling SrF in the ODT, though it performed as well as optimized \( \Lambda \) cooling in free space.

For the optimal values of \( \delta_R \) and \( R_{1↑,1↓} \), we find that \( T \sim 20 \mu \text{K} \) is regularly achievable. However, we have observed that \( T \) is sensitively dependent on the spatial alignment of the \( \Lambda \)-cooling beams. By iteratively adjusting the alignment while optimizing for \( T \), we were able to achieve a minimum of \( T = 14(1) \mu \text{K} \) (Fig. 3c). Because this optimal condition was difficult to maintain, the SrF cloud had the more typical temperature in the data shown throughout this paper.

Next, we studied the dependence of number of trapped molecules, \( N_{ODT} \), on trap depth (Fig. 4(a)). This is important because we want to capture as many molecules as possible, so we must ensure that our trap is deep enough to saturate \( N_{ODT} \). Furthermore, it was observed that the trap loading efficiency of CaF molecules peaked for \( T_D \sim 130 \mu \text{K} \) [15], and thus we wanted to check if SrF loading had similar behavior. For this measurement, we recapture and image the optically trapped molecules in an rMOT. This is done by turning on the rMOT coils and switching from the \( \Lambda \)-cooling laser configuration to the rMOT configuration. After the ODT is loaded, but prior to the rMOT recapture, we turn off all cooling light for \( t_{sh} = 140 \mu \text{s} \) to ensure that untrapped molecules fall out of the MOT capture volume and are not detected.

We find that \( N_{ODT} \) rises monotonically with trap depth, but appears to saturate for \( T_D \gtrsim 500 \mu \text{K} \). We suspect that this striking difference in behavior, relative to CaF, relates to which states are chosen for \( \Lambda \)-cooling. Hyperfine induced mixing between \( |1,1/2 \rangle \) and \( |1,3/2 \rangle \) modifies the transition strengths from the \( |\Pi_{1/2},J=1/2 \rangle \) hyperfine states to these levels. In SrF, the \( |1,3/2 \rangle \) state couples \( 56\times \) more strongly to \( |\Pi_{1/2},J=1/2, F=0 \rangle \) than to \( |\Pi_{1/2},J=1/2, F=1 \rangle \) [49], so we expect that the \( \Lambda \) system primarily couples through the former. This avoids any complications that may arise due to the large vector light shift in the \( |\Pi_{1/2},J=1/2, F=1 \rangle \) state [49]. If the \( |2,3/2 \rangle \) and \( |1,1/2 \rangle \) states are used, as in CaF [15], the coupling must be through \( |\Pi_{1/2},J=1/2, F=1 \rangle \). The larger number of sublevels, all of which experience differential shifts, in the latter scheme may also limit the effectiveness of \( \Lambda \)-cooling in deeper ODTs.

Another critical trap quantity is the lifetime \( \tau_{ODT} \). In order to study SrF collisions, we will need \( \tau_{ODT}^{-1} \lesssim \beta n \), where \( \beta \) is a collisional rate coefficient. We measure \( \tau_{ODT} \) by shutting the \( \Lambda \)-cooling light for a variable time before re-opening the shutter and imaging the remaining trapped molecules. We find \( \tau_{ODT} = 910(200) \mu \text{s} \) (Fig. 4(b)). Since this is comparable to the lifetime we
measure in a magnetic quadrupole trap with the same background pressure [13], it seems likely that the lifetime in both cases is limited by collisions with background gas.

We also measure the lifetime of molecules in the ODT while Λ-cooling light is applied, $\tau_\Lambda$. This quantity sets the time over which molecule loading is effective and over which in-situ imaging can occur. To measure $\tau_\Lambda$, we continuously apply the Λ light for an additional $t_c = 650\,\text{ms}$ after the $150\,\text{ms}$ loading and $50\,\text{ms}$ release times, and image for $50\,\text{ms}$ intervals during $t_c$.

We measure $\tau_\Lambda = 290(50)\,\text{ms}$, similar to what was observed in an ODT of CaF [15]. In that experiment, the increased loss observed in presence of Λ light was attributed to spatial diffusion out of the trap induced by scattering events. However, Monte Carlo simulations indicate that this should contribute negligibly to the SrF loss rate at our ratio of $T_D/T$. Light-assisted collisions represent another potential loss mechanism. Λ-light assisted loss rate coefficients of $\beta \geq 10^{-9}\,\text{cm}^3\,/\text{s}$ have been observed in diatomic molecules held in optical tweezers [19], so this effect could plausibly limit lifetimes to the few $100\,\text{ms}$ level for our typical peak density of $10^9\,\text{cm}^{-3}$.

For applications where high-fidelity detection is critical, such as studying molecules prepared in arrays of optical tweezers [17, 19], it is important to scatter large numbers of photons per molecule. The detection efficiency increases with the average number of photons emitted per molecule during one imaging lifetime, $t_\lambda R_\lambda$, where $R_\lambda$ is the scattering rate during Λ-cooling. We measure $R_\lambda = 3.1 \times 10^9\,\text{s}^{-1}$ by comparing the fluorescence collected with that from the MOT recapture, where the scattering rate is known [8]. Thus, $t_\lambda R_\lambda = 9(2) \times 10^4$, ~3 times larger than demonstrated in an ODT of CaF [15] despite the similar $t_\lambda$. We attribute the larger $R_\lambda$ observed here to the smaller in-trap detuning ($\Delta_{\text{trap}} / \Gamma = 1.5$ here compared to $\Delta_{\text{trap}} / \Gamma = 3.6$ in [15]).

In conclusion, by optimizing the combination of trap light polarization and intensity imbalance of Λ-enhanced gray molasses lasers, we have loaded ~5% of SrF molecules from our rMOT into a $T_D = 570\,\mu\text{K}$ deep ODT, at temperatures as low as $T = 14(1)\,\mu\text{K}$. The large value of the ratio $T_D / T$ implies strong compression of the molecular cloud, yielding density and phase space density higher than previously reported in bulk gases of directly cooled molecules, despite starting with 10 times fewer molecules.

We find that several features of loading molecule ODTs using Λ-cooling remain poorly understood, such as the dependence on the ratio of Λ light intensities, the observed interplay between the trap polarization and cooling light intensity imbalance, and, more generally, the effect of vector and tensor light shifts. Once these features are better understood, it is possible that higher trap compression could be achieved.

We are currently working on ways to increase both the number of molecules in our rMOT and the loading efficiency into the ODT. For the high compression achieved in our trap, a factor of 5 increase in $N_{\text{ODT}}$ would result in a universal-rate collision loss rate [56], $\tau_0 = (\beta n)^{-1} \sim \tau_{\text{ODT}}$. This would be sufficient to allow collisions of ultracold SrF molecules to be studied for the first time.

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Supplemental Material: Polarization Enhanced Deep Optical Dipole Trapping of $\Lambda$-cooled Polar Molecules

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We determine the AC Stark Hamiltonian resulting from monochromatic light of intensity $I$ and frequency $\omega_L$ at a given polarization $\hat{p}$ through second order perturbation theory. We find that the matrix elements of the effective AC Stark Hamiltonian for two sublevels $|i_1\rangle$, $|i_2\rangle$ within the same rovibronic state $|i\rangle$ can be written as:

$$\langle i_1 | H_{AC} | i_2 \rangle = -\frac{I}{2c\hbar \epsilon_0} \sum_f \left( \frac{d_{fi}^2}{\omega_{fi} - \omega_L} + \frac{d_{fi}^2}{\omega_{fi} + \omega_L} \right) \langle i_1 | \hat{r} \cdot \hat{p} | f \rangle \langle f | \hat{r} \cdot \hat{p} | i_2 \rangle$$  \hspace{1cm} (S1)$$

where we consider specifically the AC Stark Hamiltonians for two values of $|i\rangle$; $|i\rangle = |X^2\Sigma, v = 0, N = 1\rangle$ and $|i\rangle = |A^2\Pi_{1/2}, v = 0, J = 1/2\rangle$, $f$ refers to all other states, $\omega_{fi} = \omega_f - \omega_i$ where $\hbar \omega_f$ ($\hbar \omega_i$) are the energies of state $|f\rangle$ ($|i\rangle$), $d_{fi} = \langle f | er | i \rangle$ is the transition dipole matrix element, and we have included the co-rotating term. In Table S1 we list the molecule-frame transition dipole matrix elements we use for calculating the AC Stark shift.
AC Stark shift from ODT for $|i⟩ = |X^2Σ, N = 1⟩$

First we consider the case where $|i⟩ = |X^2Σ, N = 1⟩$.

To calculate the $⟨f|\hat{r} \cdot \hat{p}|i⟩$ terms when $f$ is a $|Π⟩$ state (e.g. Hund’s case (a)) we first express $|X^2Σ, N = 1⟩$ (Hund’s case (b): $|F', N', J', m_F'⟩$) in the Hund’s case (a) basis [60]

$$|Λ; N, S, J⟩ = \sum_{Ω=−1/2}^{1/2} \sum_{Σ=−1/2}^{1/2} (−1)^{J+Ω}\sqrt{2N+1} \begin{pmatrix} S & N & J \\ Σ & Λ & −Ω \end{pmatrix} |Λ, S, Σ, Ω, J⟩$$ (S2)

We then follow the method in the appendix of [61] to evaluate $|⟨f|\hat{r} \cdot \hat{p}|i⟩|^2$ for a particular set of quantum numbers $\{F', J', m_F'\}$ for state $|i⟩$.

When $|f⟩$ is a $|Σ⟩$ (case (b) ($|f; F, N, J, m_F⟩$)) state, we determine:

$$|⟨f|\hat{r} \cdot \hat{p}|i⟩| = m_1 m_2 m_3 m_4$$ (S3)

where

$$m_1 = (−1)^{F−m_F} \begin{pmatrix} F & 1 & F' \\ −m_F & −p & m_F' \end{pmatrix}$$

$$m_2 = (−1)^{F'+J+1+I} \sqrt{(2F+1)(2F'+1)} \begin{pmatrix} J' & F' & I \\ F & J & 1 \end{pmatrix}$$

$$m_3 = (−1)^{J'+N+1+S} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} N' & J' & S \\ J & N & 1 \end{pmatrix}$$

$$m_4 = (−1)^N \sqrt{(2N+1)(2N'+1)} \begin{pmatrix} N & 1 & N' \\ 0 & 0 & 0 \end{pmatrix}$$ (S4)

and $p$ refers to a polarization component of the ODT, $p = \{0, ±1\} = \{π, σ^±\}$.

In Table S2, we show the solution of Eq. S1 for $\hat{p} = σ^+$ for the allowed values of $|X^2Σ; N = 1, F, m_F⟩$ for $I = 2.08$ MW/cm$^2$ (the peak intensity of the ODT). We note here that, throughout, we write energies $E$ in units either of angular frequency ($ω = E/\hbar$), temperature ($T = E/k_B$), or wavenumber ($k = E/(2πhc)$).
The AC Stark Hamiltonian can be written in terms of a scalar \( (\alpha_s) \), vector \( (\alpha_v) \), and tensor \( (\alpha_T) \) polarizability [62]. For an \( |F = 1\rangle \) state this is, in the \( |F, m_F\rangle \) basis

\[
\begin{align*}
\frac{H_{\text{Stark}}}{E_s} = & \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix} - \frac{\alpha_v}{\alpha_s} \begin{pmatrix}
-\sin(2\gamma_{\text{ODT}}) & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & \sin(2\gamma_{\text{ODT}})
\end{pmatrix} \\
& - \frac{\alpha_T}{\alpha_s} \begin{pmatrix}
\frac{1}{2} & 0 & \frac{3}{2} \cos(2\gamma_{\text{ODT}}) \\
0 & -1 & 0 \\
\frac{3}{2} \cos(2\gamma_{\text{ODT}}) & 0 & \frac{1}{2}
\end{pmatrix}
\end{align*}
\]
where \( E_s \) is the scalar Stark shift (equal to the shift for \(|0,0\rangle\), and also to the average shift over all \(|F,m\rangle\) states, in Table S2). Even though the two \(|F = 1\rangle\) states are the ones that we couple in our \( \Lambda \)-system, the molecule has a non-trivial probability of occupying the \(|F = 2\rangle\) state during the cooling process, and so the Stark shifts in that level may also play some role in how the cooling performs. For \(|F = 2\rangle\), we find:

\[
\frac{H_{\text{Stark}}}{E_s} = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{pmatrix} - \frac{\alpha_V}{\alpha_S} \begin{pmatrix}
-\sin(2\gamma_{\text{ODT}}) & 0 & 0 & 0 & 0 \\
0 & -\frac{\sin(2\gamma_{\text{ODT}})}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\sin(2\gamma_{\text{ODT}})}{2} \\
0 & 0 & 0 & 0 & \sin(2\gamma_{\text{ODT}})
\end{pmatrix}
\]

\[
-\frac{\alpha_T}{\alpha_S} \begin{pmatrix}
\frac{1}{2} & 0 & \sqrt{\frac{3}{8}} \cos(2\gamma_{\text{ODT}}) & 0 & 0 \\
0 & -\frac{1}{4} & 0 & \frac{3}{4} \cos(2\gamma_{\text{ODT}}) & 0 \\
\sqrt{\frac{3}{8}} \cos(2\gamma_{\text{ODT}}) & 0 & -\frac{1}{2} & 0 & \sqrt{\frac{3}{8}} \cos(2\gamma_{\text{ODT}}) \\
0 & \frac{3}{4} \cos(2\gamma_{\text{ODT}}) & 0 & -\frac{1}{4} & 0 \\
0 & 0 & \sqrt{\frac{3}{8}} \cos(2\gamma_{\text{ODT}}) & 0 & \frac{1}{2}
\end{pmatrix}
\]

(S6)

For \( p = \pm 1 \) (\( \gamma_{\text{ODT}} = \pm 45 \)) these Hamiltonians are diagonal. So, the ratios of \( \alpha_V/\alpha_S \) and \( \alpha_T/\alpha_S \) can be determined directly from column 2 of Table. S2, and are displayed in the fourth and fifth columns of that table.

Plugging those values into Eq. S5 and Eq. S6 and solving for the eigenvalues as a function of \( \gamma_{\text{ODT}} \), we find the curves shown in Fig. 2(f) in the main text for the two \(|F = 1\rangle\) states, along with those in Fig. S1(a) for the \(|F = 2\rangle\) state.

**AC Stark shift from ODT beams for \(|i\rangle = |A^2\Pi_{1/2}, J = 1/2\rangle\)**

The ODT also induces AC Stark shifts in the \(|A^2\Pi_{1/2}, J = 1/2\rangle\) state. In Table S1 we show the additional transition dipole matrix elements needed to calculate the AC Stark shifts for this level. By calculating \( \alpha_S \) and \( \alpha_V \) (\( \alpha_T = 0 \) for this state) in the same manner as we did above for \(|X^2\Sigma, N = 1\rangle\), we can determine the eigenenergies of the AC Stark matrix in this state vs \( \gamma_{\text{ODT}} \) (Fig. S1(b)).
FIG. S1. (a) Solid lines are eigenenergies of the AC Stark Hamiltonian in the $|X^2\Sigma, N = 1, F = 2\rangle$ manifold from solving Eq. S6 for $\lambda = 1064\, \text{nm}$ and $I = 2.0\, \text{MW/cm}^2$ as a function of $\gamma_{ODT}$ for the determined values of $\alpha_T$ and $\alpha_V$ in the $F = 2$ level. Black dashed line is $E_s$. (b) Eigenenergies of the AC Stark Hamiltonian for the $|A^2\Pi_{1/2}, J = 1/2\rangle$ state under the same conditions as (a). Because the tensor polarizability $\alpha_T = 0$ in this state, the Hamiltonian is diagonal in the $|F, m_F\rangle$ basis. For (b), blue corresponds to $|F = 1, m_F = +1\rangle$, green to $|F = 1, m_F = -1\rangle$, and red to both $|F = 0, m_F = 0\rangle$ and $|F = 1, m_F = 0\rangle$.

**AC Stark shift from $\Lambda$-cooling beams for $|i\rangle = |X^2\Sigma, N = 1\rangle$**

To estimate whether the differential AC Stark shifts resulting from the $\Lambda$-cooling lasers could be large enough to compensate for those from the ODT, we solve for the AC Stark shifts resulting from a 1D pair of counter-propagating cross-circularly-polarized $\Lambda$ beams with one photon detuning $\Delta/(2\pi)$ equivalent to the ‘in-trap’ value (e.g. with the ODT induced Stark shifts for the $X$ (Fig. 2(f) of the main text) and $A$ (Fig. S1(b)) states added in) of 10 MHz, $\delta_R/(2\pi) = 1.2\, \text{MHz}$, $R_{1\uparrow,1\downarrow} = 2/3$, $R_{IA} = 0.74$, and the beam intensity (summed over both hyperfine addressing frequency components) of the initial (stronger) pass is 46 mW/cm$^2$, matching the experimental conditions described in the paper.

We found that $\langle F = 1 \downarrow, m_F = -1|H_{AC}/(2\pi)|1 \downarrow, -1\rangle - \langle 1 \downarrow, +1|H_{AC}/(2\pi)|1 \downarrow, +1\rangle = 205\, \text{kHz}$ and $\langle 1 \uparrow, -1|H_{AC}/(2\pi)|1 \uparrow, -1\rangle - \langle 1 \uparrow, +1|H_{AC}/(2\pi)|1 \uparrow, +1\rangle = 140\, \text{kHz}$ ($m_F$ remains a good quantum number in the presence of only circularly polarized light). These differential shifts are comparable to the ones induced by the ODT (Fig. 2(f) of the main text) when $\gamma_{ODT} = \pm 45^\circ$, and so could conceivably play a role in either mitigating or enhancing the effect of differential intra-hyperfine manifold shifts on the in-trap gray-molasses cooling.
FIG. S2. A-coupling diagram for the $|A^2\Pi_{1/2}, J=1/2, F'=0\rangle \leftrightarrow |X^2\Sigma, N=1, F, J\rangle$ transition for the case of $\sigma^+$ polarized light. Values next to the arrows indicate $f_{F,F'}$. Left: $F'=0$, Right: $F'=1$.

Differential Transition Strengths and Two Photon Rabi Frequency for $\Lambda$-cooling

In the main text we implied that the $\Lambda$-cooling light primarily couples the $|X\Sigma, F=1\uparrow\rangle$ and $|X\Sigma, F=1\downarrow\rangle$ states through the $|A\Pi, F'=0\rangle$ manifold and not the $|A\Pi, F'=1\rangle$ manifold. Here, we justify that assumption by considering the simple scenario for when the two manifolds are coupled by $\sigma^+$ polarized light. In Figure S2 we illustrate the branching ratios for decays from the $|A\Pi, F'\rangle$ manifold to the $|X\Sigma, F\rangle$ manifold, $f_{F,F'}$, which are proportional to the squares of transition dipole matrix elements, for states that are coupled by the $\sigma^+$ $\Lambda$-cooling light.

The two photon Rabi frequency, for the case when the amplitude through a single excited state $F'$ dominates, is given by:

$$\Omega_{F'} = \frac{\Gamma^2}{4\Delta} \sqrt{f_{\uparrow,\uparrow,F'} f_{\downarrow,\downarrow,F'}} \sqrt{\frac{I_{\uparrow,\uparrow,F'} I_{\downarrow,\downarrow,F'}}{I_{sat}^2}}$$  \hspace{1cm} (S7)

where $I_{F,F'}$ refers to the intensity of the light driving the transition between states $|X\Sigma, F\rangle$ and $|A\Pi, F'\rangle$, and $I_{sat} = \pi hc\Gamma/(3\lambda^2) \ (\lambda = 663 \text{ nm for this transition})$ is the saturation intensity ($I_{sat} = 2.9 \text{ mW/cm}^2$). Inserting the $f_{F,F'}$ values shown in Fig. S2, the in-trap overall detuning $\Delta/(2\pi) = 10 \text{ MHz}$, and the intensity (278 mW/cm$^2$) and hyperfine ratio $R_{1\uparrow,1\downarrow} \ (2/3)$, used in the experiment into Eq. S7, we find $\Omega_0/(2\pi) = 8.5 \text{ MHz}$ and $\Omega_1/(2\pi) = 2.1 \text{ MHz}$ for each of the two $F'=1$ coupled states, justifying the assumption that the hyperfine levels are primarily coupled through $F'=0$. The disparity in two-photon Rabi frequencies is primarily due to the extraordinarily low branching ratio between $|A\Pi, F'=1\rangle$ and $|X\Sigma, F=1 \uparrow\rangle$ of $f_{\uparrow,1} = 0.0047$. We find that $\Omega_0/(2\pi)$ is similar to the width of the
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