Magneeto–optical trapping of a diatomic molecule

J. F. Barry†, D. J. McCarron†, E. B. Norrgard†, M. H. Steinecker† & D. DeMille†

Laser cooling and trapping are central to modern atomic physics. The most used technique in cold-atom physics is the magneto-optical trap (MOT), which combines laser cooling with a restoring force from radiation pressure. For a variety of atomic species, MOTs can capture and cool large numbers of particles to ultracold temperatures (less than ~1 millikelvin); this has enabled advances in areas that range from optical clocks to the study of ultracold collisions, while also serving as the ubiquitous starting point for further cooling into the regime of quantum degeneracy. Magneto-optical trapping of molecules could provide a similarly powerful starting point for the study and manipulation of ultracold molecular gases. The additional degrees of freedom associated with the vibration and rotation of molecules, particularly their permanent electric dipole moments, allow a broad array of applications not possible with ultracold atoms. Spurred by these ideas, a variety of methods has been developed to create ultracold molecules. Temperatures below 1 microkelvin have been demonstrated for diatomic molecules assembled from pre-cooled alkaline atoms, but for the wider range of species amenable to direct cooling and trapping, only recently have temperatures below 100 millikelvin been achieved. The complex internal structure of molecules complicates magneto-optical trapping. However, ideas and methods necessary for creating a molecular MOT have been developed recently. Here we demonstrate three-dimensional magneto-optical trapping of a diatomic molecule, strontium monofluoride (SrF), at a temperature of approximately 2.5 millikelvin, the lowest yet achieved by direct cooling of a molecule. This method is a straightforward extension of atomic techniques and is expected to be viable for a significant number of diatomic species. With further development, we anticipate that this technique may be employed in any number of existing and proposed molecular experiments, in applications ranging from precision measurement to quantum simulation and quantum information to ultracold chemistry.

In laser cooling, the species of interest is illuminated by counter-propagating pairs of laser beams. The laser frequency is detuned just below resonance with an electronic transition. Owing to the Doppler effect, a particle is more likely to absorb a photon from the beam that opposes the particle velocity, slowing the particle. If the subsequent spontaneous emission returns the particle to the same initial state (or another state also excited by the lasers), then this process of absorption and spontaneous emission can be repeated many times (a ‘cycling transition’). This provides a damping force. However, this force does not act to spatially confine the particles. In a MOT, cooling and confinement are produced simultaneously. Three orthogonal pairs of laser beams are spatially overlapped with a quadrupole magnetic field. For a pair of ground and excited state Zeeman sublevels, a deviation from the trap centre generally induces a Zeeman shift that moves the transition closer to or further from resonance with the lasers. For a small deviation along a given laser axis, the transition shifted closest to resonance can be driven by a particular laser polarization; this polarization is chosen for the laser counter-propagating to the direction of the deviation, while the co-propagating laser has the orthogonal polarization. Hence, on average there is a confining force restoring particles towards the centre of the trap.

The SrF MOT described in this work uses techniques very similar to those used for standard atomic MOTs. Anti-Helmholtz coils create a static quadrupole magnetic field (with an axial field gradient, dFz/dz, equal to twice the radial field gradient, dFz/dR), and pairs of circularly polarized laser beams pass through the centre of this field along three orthogonal axes. The trap is loaded with pulses of SrF from a cryogenic buffer gas beam source that have been slowed using radiation pressure. However, the level structure of SrF dictates that our MOT is similar to a rarely used and poorly understood configuration of atomic MOT (known as type II), which differs in certain characteristics from the most common atomic MOTs (type I).

The type-I MOT employs an F→F = F + 1 cycling transition, where F is the total angular momentum quantum number and the prime indicates the excited state. For a given polarization, particles in all ground-state Zeeman sublevels are optically coupled to the excited state (all states are ‘bright’). The type-II MOT operates on an F→F′ = F′ – 1 transition, where certain ‘dark’ ground state sublevels are not optically coupled to the excited state. The presence of dark states reduces the spontaneous photon scattering rate; this rate can go to zero in the absence of a mechanism to ‘remix’ dark states with the bright states. Moreover, scattering alone does not ensure a confining force; the scattering rate from the laser counter-propagating to a particle’s deviation from the trap centre must exceed the scattering rate from the laser co-propagating. In type-II systems, the level structure makes it possible for particles to be pumped into a state dark to the counter-propagating laser but bright to the co-propagating laser, so a confining force is not guaranteed. Consequently the damping rate and restoring force may be significantly smaller for type-II MOTs than for those of type I. There appears to be no widely accepted understanding of the mechanisms responsible for generating a restoring force in type-II MOTs. Nevertheless, type-II MOTs have been demonstrated in several atomic systems; for these, relatively weak confinement and slightly elevated temperature are typically observed. The rotational structure of diatomic molecules generically requires their cycling transitions to correspond to a type-II MOT system; the SrF MOT described here is hence also of type II.

We use a previously demonstrated scheme for creating a cycling transition in SrF (refs 8–10) on the X2Σ+ → A1Π1/2 electronic transition (see Methods). Calculated vibrational branching fractions bv,v′, for decay of the excited state with vibrational quantum number v′ to the ground state with vibrational quantum number v, suggest that only three vibrationally excited levels in the X state (v′ = 1, 2, 3) are significantly populated after ~106 photon scattering events, corresponding to ~1 s of optical cycling for typical scattering rates (see below). Hence, three vibrational repumping wavelengths are expected to be sufficient to trap SrF for the ~1 s timescale typical of atomic MOTs. We denote the laser addressing the X(v = i) → A(v′ = j) transition by Lij, so that the three repump lasers are labelled L10, L21 and L32; the primary and secondary trapping lasers are denoted L00 and L10 respectively. (The need for a secondary trapping laser is explained below.) Radio-frequency sidebands on the L10, L21 and L32 lasers address spin-rotation/hyperfine (SR/HF) substructure in the X2Σ+ state (Fig. 1a). Rotational branching is eliminated by driving an N = 1(J = 3/2, 1/2) → J′ = 1/2 transition, where N is the total angular momentum excluding electronic and nuclear spin and J is the total angular momentum excluding nuclear spin. Driving these transitions optically pumps population into dark ground-state.
Zeeman sublevels not excited by the laser\textsuperscript{22}. These dark states must be remixed with the bright states for cycling to continue. In this work, remixing occurs both due to Larmor precession in the quadrupole magnetic field and due to optical pumping as molecules move through the complicated optical polarization gradients arising from the orthogonal pairs of circularly polarized laser beams\textsuperscript{22}.

The optimal polarization of the trapping light depends both on the sign of the difference in magnetic moment between the ground and excited states of the cycling transition and on the orientation of the quadrupole magnetic field. Within the sublevels of the SrF X\(^2\Sigma(N = 1)\) state, two of the four Sr/HF manifolds have positive magnetic g-factors, one has g = 0, and the remaining manifold has g < 0 (Fig. 1a); the \( ^2\Sigma^+_{1/2} \) state has g = 0. The presence of both negative and positive g-factors means that laser frequencies addressing the different Sr/HF manifolds must have different polarizations for optimal trapping. This is achieved by combining the \( L_{00} \) light with single-frequency light of the opposite polarization from the \( L_{10} \) secondary trapping laser (see Methods).

The pulse of molecules from the beam source begins with laser ablation of an SrF\(_2\) target at \( t = 0 \) ms. The slowing is applied from \( t = 0 \) ms to \( t = 40 \) ms (see Methods). Molecules in the trapping region are detected via laser-induced fluorescence (LIF) from the X \( \rightarrow \) A cycling transition at \( \lambda_{00} = 663.3 \) nm and imaged onto a CCD (Fig. 1b; see Methods).

Realization of magneto-optical trapping results in increased LIF from a small area in the trapping region near the B-field axis of SrF\(_2\). This localized LIF persists for an increased duration compared to the spatially broad LIF from the untrapped, slower molecular beam and suggests that molecules are confined in this region. To observe the MOT, the \( L_{00}, L_{10}, L_{21}, \) and \( L_{31} \) lasers must be present with the proper detunings (and, for the trapping lasers, polarizations), the B-field gradient must be present \((\partial B_z/\partial x \neq 0)\) and the laser slowing must be applied. The \( L_{31} \) laser is not necessary to observe the MOT but results in increased LIF. Maximum LIF is observed with the laser detunings \( \Delta_{00} = \Delta_{10} = -1.2 \Gamma = 2 \pi \times 8 \) MHz (where \( \Gamma = 2 \pi \times 7 \) MHz is the natural linewidth) and \( \partial B_z/\partial x = 15 \) G cm\(^{-1}\) (see Methods); these parameters are similar to those for standard atomic MOTs. Unless stated otherwise, measurements are made with these default parameters.

The proper polarization for the trapping light depends on the sign of \( \partial B_z/\partial x \). Reversing either the sign of \( \partial B_z/\partial x \) or the circular polarization of the MOT trapping light should create an anti-restoring force and prevent MOT formation. Reversing both the sign of \( \partial B_z/\partial x \) and the polarization in tandem, however, should return the system to a restoring configuration, and the MOT should be realized again. We observe the expected behaviour for these four states of the system as shown in Fig. 2, confirming magneto-optical trapping of SrF\(_2\) molecules. From these images we also determine the MOT cloud position and size by fitting the LIF intensity profile to a two-dimensional Gaussian; we find typical 1 ms widths of \( \rho_{rms} = 4.1(1) \) mm (radial) and \( z_{rms} = 2.6(1) \) mm (axial).

To probe the confining and damping forces in the MOT, the molecular cloud’s response to a rapid displacement of the trap centre is measured. During loading, a magnetic bias field offsets the MOT centre radially, along the axis of the molecular beam. The bias field is then switched off, releasing the trapped molecules into the unbiased potential. Using a short camera exposure (\( \Delta t_{exp} = 5 \) ms), the molecular cloud’s position is measured as a function of time (Fig. 3a; see Methods). The cloud exhibits damped harmonic motion as it moves towards the equilibrium position, with oscillation frequency \( \omega_z = 2 \pi \times 17.2(6) \) Hz and damping coefficient \( \alpha/m_{SrF_2} = 140(10) \) s\(^{-1}\), where \( m_{SrF_2} \) is the mass. With the measured radial width \( \rho_{rms} \), the equipartition theorem is used to find the radial MOT temperature: \( T_r = \rho_{rms}^2/m_{SrF_2} \), where \( k_B \) is the Boltzmann constant. If we assume the relation \( \alpha^2 = 2\omega_z^2 \) holds, for a standard atomic MOT in a quadrupole field\textsuperscript{14}, we find the axial oscillation frequency \( \omega_z = 2 \pi \times 24.3(9) \) Hz. The measured MOT axial width \( z_{rms} \) then corresponds to an axial temperature \( T_z = 2.0(1) \) mK.

To verify the MOT temperature, ballistic expansion measurements are performed. Trapped molecules are released at \( t_{exp} = 90 \) ms (by extinguishing the \( L_{31} \) laser). After a time of flight \( \Delta t_{TOF} \), the \( L_{31} \) light is restored, and the resulting LIF is imaged onto the CCD. A short imaging time \( \Delta t_{exp} = 5 \) ms is used to accurately determine the expanded cloud’s size.
(which is an average over the camera exposure duration) at the start time of imaging/illumination. Monte Carlo simulations for the measured trap frequencies suggest that the cloud continues to expand during the short illumination interval, and therefore the extracted width is an upper bound for the actual width at the imaging time, \( t_{\text{im}} = t_{\text{TOF}} + \Delta t_{\text{TOF}} \). Hence this treatment of the data yields upper limits on the MOT temperature. The fits give \( T_x \leq 2.7(3) \) mK and \( T_z \leq 2.1(1) \) mK, with trap frequencies \( \omega_x = 2\pi \times 19(1) \) Hz and \( \omega_z = 2\pi \times 29(1) \) Hz, corresponding to spring constants \( k_x = 2.5(3) \times 10^{-2} \) N m\(^{-1}\) and \( k_z = 5.9(4) \times 10^{-2} \) N m\(^{-1}\). These values are in good agreement with the values from the MOT oscillation measurement. The temperatures are an order of magnitude greater than the SrF Doppler temperature, \( T_D = \hbar/(2k_B) = 160 \) mK. Temperatures well above the Doppler temperature are also reported in work with atomic type-II MOTs\(^2\). These spring constants are two to three orders of magnitude smaller than for typical type-I atomic MOTs\(^2\) and approximately one order of magnitude smaller than reported values for atomic type-II MOTs\(^3\), though measurements of the spring constants in type-II atomic MOTs are so few that 'typical' behaviour is difficult to characterize. A third measurement of the MOT temperature \( T_{\text{MOT}} \) is performed using the release-and-recapture method, yielding a temperature in good agreement with the other methods (see Methods).

Measurement of the spontaneous photon scattering rate for trapped molecules, \( R_{\text{sc}} \), allows the number of trapped molecules \( N_{\text{MOT}} \) to be determined via fluorescence detection. We find \( R_{\text{sc}} = 4.3(1.4) \times 10^4 \) s\(^{-1}\) (see Methods). Based on the efficiency of the LIF detection system, measured to be \( \sim 0.8\% \), the MOT population is estimated at \( N_{\text{MOT}} = 300 \) SrF molecules, corresponding to a peak trap density of \( n_{\text{MOT}} \approx 600 \) cm\(^{-3}\).

The MOT lifetime, \( \tau_{\text{MOT}} \), is obtained by measuring LIF in the trapping region as a function of time and fitting a single exponential decay curve to the data after \( t = 67 \) ms, as shown in Fig. 3c. This time avoids significant contributions to the LIF signal from the slowed but ultimately untrapped part of the molecular beam. We find \( \tau_{\text{MOT}} = 56(4) \) ms, significantly shorter than is typically seen in atomic MOTs. When the \( \ell_{32} \) repump laser is not present, \( \tau_{\text{MOT}} = 27(2) \) ms. We have verified that neither collisions with ballistic helium from the buffer-gas beam nor collisions with background gases are the primary loss mechanism from the trap. Optical pumping into the dark \( X^2\Sigma (v = 4) \) state would result in \( \tau_{\text{MOT}} \approx 1 \) s for the measured value of \( R_{\text{sc}} \), and off-resonant excitation populating dark rotational levels is found to be insignificant (see Methods).

The strikingly low restoring force measured suggests another explanation for the low value of \( \tau_{\text{MOT}} \); the trap depth is not large compared to \( k_B T_{\text{MOT}} \), as in typical atomic MOTs, so a significant fraction of molecules (see Methods). For an initial Gaussian spatial distribution and a Boltzmann distribution of velocities (with no correlation between position and velocity), the widths \( \rho_{\text{rms}} \) and \( \rho_{\text{rms}} \) of the expanding cloud are given by:

\[
\rho_{\text{rms}}^2 = \frac{k_B T_x}{m_{\text{SrF}}} \left( \frac{1}{\omega_x^2} + (\Delta t_{\text{TOF}})^2 \right) \quad \text{and} \quad \rho_{\text{rms}}^2 = \frac{k_B T_z}{m_{\text{SrF}}} \left( \frac{1}{\omega_z^2} + (\Delta t_{\text{TOF}})^2 \right)
\]

The data and associated fits are shown in Fig. 3b. The slopes of the fits give the temperatures, which are then used with the intercepts to determine \( \omega_x \) and \( \omega_z \). This treatment plots the measured cloud width

(see Methods). For an initial Gaussian spatial distribution and a Boltzmann distribution of velocities (with no correlation between position and velocity), the widths \( \rho_{\text{rms}} \) and \( \rho_{\text{rms}} \) of the expanding cloud are given by:

\[
\rho_{\text{rms}}^2 = \frac{k_B T_x}{m_{\text{SrF}}} \left( \frac{1}{\omega_x^2} + (\Delta t_{\text{TOF}})^2 \right) \quad \text{and} \quad \rho_{\text{rms}}^2 = \frac{k_B T_z}{m_{\text{SrF}}} \left( \frac{1}{\omega_z^2} + (\Delta t_{\text{TOF}})^2 \right)
\]

The data and associated fits are shown in Fig. 3b. The slopes of the fits give the temperatures, which are then used with the intercepts to determine \( \omega_x \) and \( \omega_z \). This treatment plots the measured cloud width (which is an average over the camera exposure duration) at the start time of imaging/illumination. Monte Carlo simulations for the measured trap frequencies suggest that the cloud continues to expand during the short illumination interval, and therefore the extracted width is an upper bound for the actual width at the imaging time, \( t_{\text{im}} = t_{\text{TOF}} + \Delta t_{\text{TOF}} \). Hence this treatment of the data yields upper limits on the MOT temperature. The fits give \( T_x \leq 2.7(3) \) mK and \( T_z \leq 2.1(1) \) mK, with trap frequencies \( \omega_x = 2\pi \times 19(1) \) Hz and \( \omega_z = 2\pi \times 29(1) \) Hz, corresponding to spring constants \( k_x = 2.5(3) \times 10^{-2} \) N m\(^{-1}\) and \( k_z = 5.9(4) \times 10^{-2} \) N m\(^{-1}\). These values are in good agreement with the values from the MOT oscillation measurement. The temperatures are an order of magnitude greater than the SrF Doppler temperature, \( T_D = \hbar/(2k_B) = 160 \) mK. Temperatures well above the Doppler temperature are also reported in work with atomic type-II MOTs\(^2\). These spring constants are two to three orders of magnitude smaller than for typical type-I atomic MOTs\(^2\) and approximately one order of magnitude smaller than reported values for atomic type-II MOTs\(^3\), though measurements of the spring constants in type-II atomic MOTs are so few that 'typical' behaviour is difficult to characterize. A third measurement of the MOT temperature \( T_{\text{MOT}} \) is performed using the release-and-recapture method, yielding a temperature in good agreement with the other methods (see Methods).

Measurement of the spontaneous photon scattering rate for trapped molecules, \( R_{\text{sc}} \), allows the number of trapped molecules \( N_{\text{MOT}} \) to be determined via fluorescence detection. We find \( R_{\text{sc}} = 4.3(1.4) \times 10^4 \) s\(^{-1}\) (see Methods). Based on the efficiency of the LIF detection system, measured to be \( \sim 0.8\% \), the MOT population is estimated at \( N_{\text{MOT}} = 300 \) SrF molecules, corresponding to a peak trap density of \( n_{\text{MOT}} \approx 600 \) cm\(^{-3}\).

The MOT lifetime, \( \tau_{\text{MOT}} \), is obtained by measuring LIF in the trapping region as a function of time and fitting a single exponential decay curve to the data after \( t = 67 \) ms, as shown in Fig. 3c. This time avoids significant contributions to the LIF signal from the slowed but ultimately untrapped part of the molecular beam. We find \( \tau_{\text{MOT}} = 56(4) \) ms, significantly shorter than is typically seen in atomic MOTs. When the \( \ell_{32} \) repump laser is not present, \( \tau_{\text{MOT}} = 27(2) \) ms. We have verified that neither collisions with ballistic helium from the buffer-gas beam nor collisions with background gases are the primary loss mechanism from the trap. Optical pumping into the dark \( X^2\Sigma (v = 4) \) state would result in \( \tau_{\text{MOT}} \approx 1 \) s for the measured value of \( R_{\text{sc}} \), and off-resonant excitation populating dark rotational levels is found to be insignificant (see Methods).

The strikingly low restoring force measured suggests another explanation for the low value of \( \tau_{\text{MOT}} \); the trap depth is not large compared to \( k_B T_{\text{MOT}} \), as in typical atomic MOTs, so a significant fraction of molecules...
can escape the trap simply by being in the high-energy tail of the Boltzmann distribution. The MOT trap depth $U_{\text{MOT}}$ can be estimated using $U_{\text{MOT}} = \frac{1}{2} k_B \langle d/2 \rangle^2$, assuming that $k_B$ is constant to the edges of the MOT beam ($d$ is the beam diameter). This gives $U_{\text{MOT}}/k_B = 10(1) \times 10^7 \text{K} \approx 47 \text{mK}$ in contrast to atomic MOTs where $U_{\text{MOT}}/k_B \approx 1 \text{K} \approx 1000T_{\text{MOT}}$. We presume that rapid molecule–light interactions maintain a constant temperature throughout the MOT, leading to continuous loss rather than evaporative cooling as in a conservative trap (where the trap leaves the total energy of a trapped sample unchanged). A simple model for the rate of particle escape under these conditions lends credence to this explanation for the short MOT lifetime (see Methods). Additional support comes from the observation that $T_{\text{MOT}}$ depends strongly on the MOT beam diameter (Fig. 3c, inset). Reducing the beam diameter $d_j$ from 23 mm to 21 mm (a <1% decrease in power) reduces $T_{\text{MOT}}$ by ~30%. We are unaware of any other trap loss mechanism that might exhibit this behaviour.

For our cycling transition, the maximum restoring force $F_{\text{max}} = k_d d_j/2$ corresponds to a confining photon scattering rate $R_{\text{conf}} = F_{\text{max}}/(h k) = 5(2) \times 10^4 \text{s}^{-1}$ (where $k = 2\pi n/\lambda$ is the wavenumber) confining photons from a single MOT beam, only ~1% of $R_{\text{conf}}$. The small value of $R_{\text{conf}}/R_{\text{opt}}$ may be understood qualitatively by noting that in a simple one-dimensional model, the angular momentum level structure of our system ($J = 3/2$, $1/2 \rightarrow J' = 1/2$) ensures that each photon scattered in the ‘correct’ (confining) direction on average must be followed by a photon scattered in the ‘incorrect’ (anti-confining) direction in order to resume optical cycling9. In three dimensions, with complicated polarization gradients and other means of remixing, this relation no longer holds exactly. Nonetheless, the mechanism behind the slight bias of scattering events towards the trap centre that leads to the weak, yet non-zero confining force is not well understood. This same type of level structure is also the defining characteristic of atomic type-II MOTs, which exhibit qualitatively similar characteristics to our SrF MOT (such as extended spatial extent and elevated temperature) although with reported stronger confinement10–12. Hence the weak trapping and only moderately low temperature observed in our SrF MOT are believed to be due to the angular momentum level structure rather than any other issues related specifically to using a diatomic molecule rather than an atom. Despite these limitations, our method succeeds in trapping and cooling molecules to the lowest temperature reported for any direct-cooling method to date.

Future work is expected to allow substantial increases in the density and the number of molecules trapped. For example, the trapable flux may be increased by implementing a more efficient slowing method23 or by transversely confining the molecular beam as it is slowed13. A variety of methods may enable increased trap depth by increasing the fraction of scattered photons contributing to the confining force ($R_{\text{conf}}/R_{\text{opt}}$), which could in turn increase trap lifetime, capture velocity, density, and number of molecules trapped. This could be accomplished, for example, by rapid synchronous reversing of the MOT magnetic field gradient and the laser circular polarizations, as recently demonstrated in two-dimensional magneto-optical trapping of a molecular beam14, or alternatively by using a microwave electric field to pump molecules in anti-trapped Zeeman sublevels into trapped levels by driving transitions through other rotational states8,9.

Although magneto-optical trapping of molecules is in its infancy, our results demonstrate that this technique could be applied in a straightforward way to a significant number of diatomic species27. The MOT has provided indispensable for cooling and trapping many atomic species; with further development, we expect that it may prove similarly useful for producing ultracold gases of diatomic molecules. Such an advance is expected to enable a wide range of new experiments including tests of the standard model of particle physics26,28, sensitive searches for variations of fundamental constants49, and studies of novel chemical dynamics in the ultracold temperature regime7.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

Received 22 April; accepted 23 June 2014.

Carr, L., DeMille, D., Krems, R. & Ye, J. Cold and ultracold molecules: science, technology and applications. New J. Phys. 11, 055049 (2009).

Ni, K.-K. et al. A high phase-space-density gas of polar molecules. Science 322, 231–235 (2008).

Danzi, J. G. et al. An ultracold high-density sample of rubidionic ground-state molecules in an optical lattice. Nature Phys. 6, 265–270 (2010).

Zeppenfeld, M. et al. Sisyphus cooling of electrically trapped polyatomic molecules. Nature 491, 570–573 (2012).

Stuhl, B. K. et al. Evaporative cooling of the dipolar hydroxyl radical. Nature 492, 396–400 (2012).

Di Rosa, M. D. Laser-cooling molecules. Eur. Phys. J. D 31, 395–402 (2004).

Stuhl, B. K., Sawyer, B. C., Wang, D. & Ye, J. Magneto-optical trap for polar molecules. Phys. Rev. Lett. 101, 243002 (2008).

Shuman, E. S., Barry, J. F., Glenn, D. R. & DeMille, D. Radiative force from optical cycling on a diatomic molecule. Phys. Rev. Lett. 103, 223001 (2009).

Shuman, E. S., Barry, J. F. & DeMille, D. Laser cooling of a diatomic molecule. Nature 467, 820–823 (2010).

Barry, J. F., Shuman, E. S., Norgard, E. B. & DeMille, D. Laser radiation pressure slowing of a molecular beam. Phys. Rev. Lett. 108, 103002 (2012).

Hummon, M. T. et al. 2D magneto-optical trapping of diatomic molecules. Phys. Rev. Lett. 110, 143001 (2013).

The ACME Collaboration. Order of magnitude smaller limit on the electric dipole moment of the electron. Science 343, 269–272 (2014).

Micheli, A., Brennen, G. K. & Zoller, P. A toolbox for lattice-spin models with polar molecules. Nature Phys. 2, 341–347 (2006).

DeMille, D. Quantum computation with trapped polar molecules. Phys. Rev. Lett. 88, 067901 (2002).

Krems, R. V. Cold controlled chemistry. Phys. Chem. Chem. Phys. 10, 4079–4092 (2008).

Hutzler, N. R., Lu, H.-I. & Doyle, J. M. The buffer gas beam: an intense, cold, and slow source for atoms and molecules. Chem. Rev. 112, 4803–4827 (2012).

Prentiss, M. G., Bigelow, N. P., Shahriar, M. S. & Hemmer, P. R. Forcing on three-level atoms including coherent population trapping. Opt. Lett. 16, 1695–1697 (1991).

Nasrav, K. et al. Magneto-optical trap operating on a magnetically induced level-mixing effect. Phys. Rev. A 64, 023412 (2001).

Prentiss, M., Cable, A., Bjorkholm, J. E., Chu, S. & Raab, E. L. Atomic-density-dependent losses in an optical trap. Opt. Lett. 13, 452–454 (1988).

Flemming, J. et al. Magneto-optical trap for sodium atoms operating on the D1 line. Opt. Commun. 135, 269–272 (1997).

Twari, V. B., Singh, S., Rawat, H. S. & Mehendale, S. C. Cooling and trapping of 85Rb atoms in the ground hyperfine F=2 state. Phys. Rev. A 78, 063421 (2008).

Berkeland, D. J. & Boshier, M. G. Destabilization of dark states and optical spectroscopy in Zeeman-degenerate atomic systems. Phys. Rev. A 65, 033413 (2002).

Rio Fernandes, D. et al. Sub-Doppler laser cooling of fermionic 40K atoms in three-dimensional gray optical molasses. Europhys. Lett. 100, 63001 (2012).

Metcalf, H. J. & van der Straten, P. Laser Cooling and Trapping (Springer, 1999).

Wallace, C. D. et al. Measurements of temperature and spring constant in a magneto-optical trap. J. Opt. Soc. Am. B 11, 703–711 (1994).

Chieda, M. A. & Eyler, E. Prospects for rapid deceleration of small molecules by optical bichromatic forces. Phys. Rev. A 84, 063401 (2011).

DeMille, D., Barry, J. F., Edwards, R. E., Norgard, E. B. & Steinke, M. H. On the transverse confinement of radiatively slowed molecular beams. Mol. Phys. 111, 1805–1813 (2013).

Hunter, L. R., Peck, S. K., Greenspon, A. S., Alam, S. S. & DeMille, D. Prospects for laser cooling of a molecular beam. Phys. Rev. A 85, 012511 (2012).

Tarbutt, M. R., Sauer, B. E., Hudson, J. J. & Hinds, E. A. Design for a fountain of YbF molecules to measure the electron’s electric dipole moment. New J. Phys. 15, 053034 (2013).

Chin, C., Flambaum, V. V. & Kozlov, M. G. Ultracold molecules: new probes on the variation of fundamental constants. New J. Phys. 11, 055048 (2009).

Acknowledgements We thank E.R. Edwards for contributions towards the construction of the experiment. We acknowledge funding from AFOSR (MURI), ARO, and ARO (MURI). E.B.N. acknowledges funding from the NSF GRFP.

Author Contributions All authors contributed to the experiment, the analysis of the results and the writing of the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to D.J.M. (daniel.mccarron@yale.edu).

©2014 Macmillan Publishers Limited. All rights reserved
METHODS

Cycling scheme and level structure. The X^2Σ^+ → A^1Π_g electronic transition employed in this work has a lifetime \( \tau_s = 1/1! = 24.1 \) ns. The vibrational branching for this excited state is shown in Extended Data Fig. 1a and dictates that only four lasers (one main cycling laser and three vibrational repump lasers) are required to cycle \( \geq 10^9 \) photons. In practice we use three repump lasers (L10, L11 and L12) at wavelengths \( \lambda_{110} = 686.0 \) nm, \( \lambda_{111} = 684.5 \) nm and \( \lambda_{112} = 684.9 \) nm, in addition to the primary and secondary trapping lasers (L60 and L50) at \( \lambda_{60} = 663.3 \) nm. The SR/HF structure for the X^2Σ^+ yields L50 and L60 (Extended Data Fig. 1c) in Extended Data Fig. 1b. To address each SR/HF manifold, the primary trap laser (L60) light and the repump laser (L10, L11 and L12) laser are phase-modulated with electro-optic modulators (EOMs). For the three repump lasers, the modulation frequency \( f_{mod} = 42.5 \) MHz is chosen so the first- and second-order sidebands address all four SR/HF transitions. The value of \( f_{mod} = 40.4 \) MHz for the L60 light is chosen to minimize the root-mean-squared (r.m.s.) value of the detuning for the upper three SR/HF levels at \( B = 0 \) G, while a separate laser (L50) addresses the lowest SR/HF level. The modulation depth \( M_{mod} = 2.6 \) for all these lasers provides equal power in each of the four near-resonant sidebands while minimizing power in other sidebands. For each repump laser, zero detuning (\( \Delta_l = 0 \)) is defined as the frequency which produces maximal LIF from the molecular beam when the light is applied (and retro-reflected) perpendicularly to the molecular beam. For the primary and secondary trapping lasers, the first relative position of \( \lambda_{60} \) is fixed 9 MHz above the highest-frequency \( \lambda_{50} \) sideband; these lasers are then scanned in tandem, and zero detuning (\( \Delta_{50} = \Delta_{60} = 0 \)) is defined in the same manner as for the repump lasers.

At the optimal trap laser detunings, \( \Delta_{50} = \Delta_{60} = 0 \), all trap laser frequencies are detuned to lower frequency than the primary JF sublevel they address. By default, all repump lasers are tuned to the field-free resonance (\( \Delta_{110} = \Delta_{111} = \Delta_{112} = 0 \)). A Breit-Rabi diagram showing the energy dependence of each sublevel versus magnetic field is shown in Extended Data Fig. 1c. The levels crossings in the range \( B = 15–25 \) G may limit the effective trap radius for a given B-field gradient since, at sufficiently high fields, the trap light frequency addressing the \( |J=3/2, F=1\rangle \) manifold becomes anti-trapping for the \( |J=3/2, F=2\rangle \) manifold. Note that other trapping/anti-trapping level crossings are located at higher magnetic bias fields.

The far-detuned primary laser (L60) is tuned to \( 663.3 \) nm, in addition to the \( 684.9 \) nm laser. To achieve a trapping region, the primary trap laser frequency is detuned to lower frequency than the primary laser frequency addressing the molecular beam. The magnetic field for the slowing is applied only when the slowing lasers are on. Radiation pressure slowing. The radiation pressure force acting on a molecule depends on the intensity and polarization of the light field, as well as the orientation of the molecule. In the case of atoms, the radiation pressure force is proportional to the square of the intensity of the light field. For molecules, the radiation pressure force is more complex, as it depends on the orientation and polarization of the light field with respect to the molecule.

MOT optimization. The optimal magnetic field gradient for the MOT is found to be \( dB/dz = 15 \) G cm\(^{-1}\); the MOT is visible between 4 and 30 G cm\(^{-1}\). The MOT is sensitive to the values of the laser detunings \( \Delta_{110} \) and \( \Delta_{112} \) (and less sensitive to the value of \( \Delta_{111} \)), as shown in Extended Data Fig. 4, but insensitive to the detunings of the \( L_{10} \) and \( L_{12} \) lasers.

The spontaneous scattering rate for trapped molecules. The spontaneous scattering rate \( R_s \) is measured by blocking the \( L_{12} \) repump laser at time \( t_b = 58.6 \) ms and observing the LIF decay constant, denoted \( t_{\sigma^{-1}} \), as molecules are optically pumped into the now-dark X^2Σ^+ state. LIF is recorded as a function of imaging start time \( t_m \), which is scanned from \( t_m = 54 \) ms to \( t_m = 62 \) ms. The finite duration of the camera exposure, \( t_{exp} = 1 \) ms, results in a recorded LIF signal \( Y(t_m) \) that is a convolution of the real instantaneous LIF intensity, denoted \( I(t_m) \), and the camera exposure time, that is:

\[
Y(t_m) = \int_{t_m}^{t_m + t_{exp}} I(t')dt'
\]

Given the comparatively long unperturbed MOT lifetime, \( t(t) \) is modelled as a linear function before the blocking of the \( L_{12} \) repump light (\( t = 54 \) ms to \( t = t_b = 57.6 \) ms), followed by (from \( t_b \)) an exponential decay plus an additional linear background term. This background term, included to account for LIF from the tail of the slowed but untrapped molecular beam, is deduced from a fit to the data from \( t = 59 \) ms to \( t = 62 \) ms. This function has the form:

\[
Y(t) = (m_{\text{MOT}} + c_{\text{MOT}}) I(t) + (D_B e^{-t/t_{\sigma^{-1}}} + m_{\text{LIF}} + c_{\text{LIF}}) \Theta(t - t_b)
\]

where \( m_{\text{MOT}} \) and \( c_{\text{MOT}} \) are the gradient and intercept respectively of the linear fit to the LIF from the MOT (background), \( D_B \) is the amplitude coefficient of the exponential decay term, and \( \Theta(t) \) denotes the Heaviside step function. From the fitted value \( t_{\sigma^{-1}} = 0.66 \pm 0.02 \) ms and the calculated vibrational branching fraction \( \beta_{04} = 0.0004 \), we estimate \( R_s = 1/(4 \beta_{04} t_{\sigma^{-1}}) = 4.3 \times 10^8 \) s\(^{-1}\). The measured scattering rate is close to the maximum scattering rate for this state, \( R_{\text{max}} = \frac{7}{10} / l_0 = 5.9 \times 10^8 \) s\(^{-1}\) (ref. 33). The value of \( R_s \) is similar to those measured in atomic MOTs. This observation suggests the possibility of producing strong confining and damping forces, roughly comparable to those in atomic MOTs, if the fraction of scattered photons contributing to the confining force can be greatly increased.

An independent measure of the scattering rate is obtained from the MOT lifetime measurements. The values of \( t_{\text{MOT}} \) with and without the \( L_{12} \) repump laser allow the rate ratio into the X^2Σ^+ state to be isolated. This, together with the vibrational branching fraction \( \beta_{04} \) into \( v = 3 \), yields a scattering rate \( R_s = 2 \times 10^8 \) s\(^{-1}\), with uncertainty of \( \pm 100\% \). To the large uncertainty in \( \beta_{04} \).

Uncertainties in the calculated vibrational branching fractions \( \beta_{ij} \) stem largely from uncertainties in the molecular constants for the A^1Π_g state used to calculate Franck-Condon factors. Although the errors in these constants are small, the resulting fractional uncertainty in calculated values of \( \beta_{ij} \) may be significant for off-diagonal
terms (v ≠ v') where Frank-Condon factors are strongly suppressed and vibrational branching fractions are small.\textsuperscript{31}

**MOT detection.** Molecules in the trapping region are detected via laser-induced fluorescence (LIF) from the X–A cycling transition at ∆ν₀ = 663.3 nm and imaged onto a CCD. The camera field-of-view encompasses the majority of the trapping region and is approximately centred on the zero of the quadrupole field. Unless otherwise noted, MOT imaging starts at time \( t_{\text{im}} = 60 \text{ ms} \) after ablation, the camera exposure duration is ∆τ\text{im} = 60 ms, and the signal is integrated over the entire camera field-of-view. The imaging start time and duration are chosen so that the vast majority of LIF recorded (∼90%) comes from trapped molecules rather than the temporal tail of the slow molecular beam pulse.

The LIF collection optics consist of a 150 mm focal-length spherical-singlet lens, followed by a F0.95 camera lens, then a 650-nm bandpass interference filter, and finally a CCD camera. The interference filter reflects all repump light at λ₁ = 686.0 nm, λ₂₁ = 685.4 nm and λ₂₂ = 684.9 nm for any angle of incidence (AOI) and transmits >99% of the λ₂ = 663.3 nm light at normal incidence; however transmission at λ₀ is reduced for AOI ≳ 23°.

Using the MOT chamber geometry and assuming the distribution of LIF from the MOT is isotropic, we calculate the geometric collection efficiency of the LIF optics to be \( n_{\text{geo}} = 1.1\% \). The amount of light reaching the CCD is further reduced by transmission losses (characterized by \( n_{\text{trans}} \)) and by AOI-dependent losses of the bandpass filter (characterized by \( n_{\text{filt}} \)).

We measure \( n_{\text{geo}} = 0.84 \) by tabulating the transmission efficiency of 663.3-nm light through each element of the collection optics at normal incidence. The value of \( n_{\text{filt}} \) is measured as follows. Light emission from the MOT is simulated by back-illuminating a thick piece of white Delrin with 663.3 nm light. The front surface of the Delrin is covered except for a 5-mm hole. This creates approximately uniform emission of light over the range of angles incident on the collection optics. The total number of photons hitting the CCD is measured in the presence of all collection optics and again with only the interference filter and CCD present. In this latter configuration, reflection of 663.3-nm light by the interference filter is negligible since all light is near normal incidence. The ratio of these two numbers is then divided by the ratio of solid angle subtended by the collection optics versus by the CCD sensor.

The ratio of solid angle subtended by the collection optics versus by the CCD sensor is then divided by the transmission losses through the lenses gives the filter transmission efficiency \( n_{\text{trans}} = 0.53 \) for 663.3-nm light.

\( \frac{N_{\text{MOT}}}{N_{\text{obs}}} = e^{D(t)/2T_{\text{exp}}} \cdot N_{\text{obs}} = 3 \times 10^5 \text{ molecules} \) \hspace{1cm} (5)

**Forced MOT oscillation.** The confining and damping forces within the MOT are measured by observing the trapped cloud’s response to a rapid displacement of the trap centre. At \( t = 0 \text{ ms} \), before the loading/slowing phase, a shim coil applies an ~4 G bias field to offset the trap centre by ∆L = 5 mm radially, downstream along the axis of the molecular beam. When this bias field is switched off at \( t_{\text{off}} = 58 \text{ ms} \), the centre-of-mass radial position of the trapped molecules exhibits damped harmonic motion described by:

\[ m_{\text{tot}} \frac{d^2 \rho}{dt^2} + g \frac{d \rho}{dt} + k_{\text{vib}} \rho = 0 \] \hspace{1cm} (6)

Assuming that the cloud is initially at rest, \( (d\rho/dt)|_{t=0} = 0 \), the centre-of-mass position versus time is given by

\[ \rho(t) = \rho_0 e^{-t/(2T_{\text{exp}})} \cos(\alpha c t) \] \hspace{1cm} (7)

where \( \rho_0 = \Delta p \) is the initial displacement and \( \alpha_{\text{obs}} = \sqrt{\alpha_c^2 - (\alpha_c/2\text{ms})^2} \) is the observed angular oscillation frequency.

**Extracting spatial information using LIF detection.** The weak confinement of the MOT is crucial in order for our LIF-based detection method to extract certain spatial information from the cloud. For the forced MOT oscillation measurement, the camera exposure duration (\( \Delta \tau_{\text{exp}} \)) must be short compared to the radial oscillation period (\( 2\pi/\alpha_\text{c} \times \text{ms} \)) to precisely determine the position of the cloud. We observe 2π/\( \alpha_\text{c} \times \text{ms} = 58(2) \text{ ms} \) and set \( \Delta \tau_{\text{exp}} = 5 \text{ ms} \); this satisfies the short exposure while also allowing the camera to collect enough LIF to accurately measure the spatial distribution.

Similarly, the ballistic expansion measurement uses a camera exposure duration \( \Delta \tau_{\text{exp}} = 5 \text{ ms} \). This duration is short compared to \( 2\pi/\alpha_\text{c} \times \text{ms} \), which avoids recapture and compression of the cloud by the trap light during illumination. The maximum time of flight used, \( \Delta T_{\text{exp}} = 7 \text{ ms} \), is capped by the imaging field-of-view rather than the LIF signal-to-noise ratio (in contrast to the case for the MOT oscillation measurement).

**Release and recapture.** In the release-and-recapture method, trapped molecules are released and then expand freely for a variable time of flight \( \Delta T_{\text{exp}} \) before the trap is turned back on, recapturing a fraction of the initial molecules that depends on their average velocity.

In order to avoid LIF from the untrapped molecular beam, the MOT is released at a fixed release time \( t = t_{\text{rel}} = 90 \text{ ms} \) and \( \Delta T_{\text{exp}} \) is varied from 0 to 50 ms. After each free expansion the MOT is recaptured at \( t = t_{\text{rel}} + \Delta T_{\text{exp}} \) and imaging begins at \( t = t_{\text{rel}} + \Delta T_{\text{exp}} + 3 \text{ ms} \) using \( \Delta T_{\text{exp}} = 30 \text{ ms} \). In contrast to the free-expansion measurement, this method uses a longer exposure time that gives enhanced sensitivity to the recaptured number of molecules but obviates any spatial information about the cloud before recapture.

A cloud temperature is determined by comparing the measured recaptured fraction to that of a Monte Carlo simulation, as a function of \( \Delta T_{\text{exp}} \). The model assumes isotropic expansion and a spherical trap volume with radius \( r_{\text{cap}} \) molecules inside this radius are assumed to be recaptured with 100% efficiency and those outside to be lost. The uncertainty in \( r_{\text{cap}} \) is a well-known limitation of the release-and-recapture method\textsuperscript{34}; we set \( r_{\text{cap}} = d/2 \) to obtain an upper limit on the isotropic temperature \( T_{\text{iso}} \). In the Monte Carlo simulation, initial velocities are drawn from a Boltzmann distribution and the effects of gravity are included. The initial spatial distribution is inferred from LIF images of the MOT, with the assumption that the MOT is radially symmetric. This procedure gives \( T_{\text{iso}} < 2.7(6) \text{ mK} \), in good agreement with the geometric mean of the axial and radial MOT temperatures derived from the MOT oscillation measurements \( T^2_{\text{exp}} = T_{\text{exp}} = 2.3(4) \text{ mK} \).

**Heating and cooling rates.** The measured value of \( R_{\text{MOT}} \) makes it possible to estimate a lower limit on the MOT heating rate (additional heating may be caused by stimulated emission, which is neglected here). This minimum heating rate is \( (dE/dt)_{\text{MOT}} = 2R_{\text{MOT}} E_{\text{res}} \), where \( E \) is the molecule energy and \( E_{\text{res}} = (h\gamma/2\mu) \text{photons}^{-1} \) is the photon recoil energy. By equating the heating rate to the rate of cooling from velocity damping, \( (dE/dt) = -2k_B T_{\text{MOT}}/m_{\text{tot}} \) (ref. 24), an independent lower limit on the damping coefficient \( z \) is obtained. We find \( z \approx 5 \times 10^{-23} \text{ kg}^{-1} \text{ s}^{-1} \), in agreement with the value from the MOT oscillation measurement.

**Diffusion lifetime.** We estimate the lifetime that would be measured for an SrF cloud in the presence of only optical molasses to cross-check the measured values of \( \gamma \) and \( T_{\text{exp}} \) (given the MOT beam diameter \( d \)) and to further verify that a trapping force (rather than simply the cooling effect of optical molasses) is necessary to explain our observations. Here the motion of the molecules is treated as Brownian motion within a viscous fluid\textsuperscript{35,36}. The position diffusion constant \( D_{\text{th}} \) is given by

\[ D_{\text{th}} = \frac{k_B T_{\text{exp}}}{m_{\text{tot}} c^2} \]
\[ \mathcal{D}_x = \frac{k_B T_{\text{MOT}}}{\tau} \]  

and, using our measured values of \( \tau \) and \( T_{\text{MOT}} \), we calculate \( \mathcal{D}_x = 1.4(3) \times 10^{-11} \text{m}^2\text{s}^{-1} \). The molasses lifetime \( \tau_{\text{mol}} \) is then given by:

\[ \tau_{\text{mol}} = \frac{d^2}{4\pi^2 \Sigma} = 10(2) \text{ ms} \]  

The calculated lifetime \( \tau_{\text{mol}} \) is in agreement with the fits to the data in the presence only of optical molasses. This lifetime is short compared to typical atomic molasses lifetimes (where \( \tau_{\text{mol}} \gtrsim 100 \text{ ms} \)) due both to the small damping coefficient \( \Sigma \) and the relatively high MOT temperature \( T_{\text{MOT}} \). Furthermore, the measured MOT lifetime \( \tau_{\text{MOT}} \approx 6 \times \tau_{\text{mol}} \) is consistent with our observations that molecules are confined in the MOT.

**MOT lifetime.** Although the measured MOT lifetime \( \tau_{\text{MOT}} = 56(4) \text{ ms} \) is short compared to those of typical atomic MOTs, the lifetime is \( \sim 5\times \) longer than the observed lifetimes of the molasses (\( \tau_{\text{mol}} = 0 \)) and damping/anti-restoring (\( \tau_{\text{damp}} \)) and \( \tau_{\text{repump}} \) (polarizations reversed) configurations which have apparent lifetimes of \( 11(1) \text{ ms} \) and \( 10(3) \text{ ms} \), respectively (see Fig. 3c). These apparent lifetimes for untrapped molecules should be taken as upper limits due to the temporal and spatial extent of the slowed molecular beam.

Before reaching the conclusion that the lifetime is limited by 'boil-off' of molecules with energy greater than the trap depth, several other possible effects that could limit the MOT lifetime were explored. For example, off-resonant excitation into the \( \Delta^2 \Sigma(v = 0, J = 3/2) \) state could lead to decay into the dark \( \Delta^2 \Sigma(v = 0, N = 3) \) state. To investigate this loss mechanism, a laser was added to repump population from the \( \Delta^2 \Sigma(v = 0, N = 3) \) state. This did not change the measured MOT lifetime, indicating that losses due to off-resonant excitations are negligible.

MOT loss may be caused by collisions with residual ballistic He from the buffer gas beam source, with background (diffuse) He, or with other gases in the trapping region. We test for attenuation by ballistic He by increasing the flow rate of He into the buffer gas beam source from the default value of \( \phi \) to standard cubic centimetres per minute (scm) to \( \phi = 20 \text{ scm} \). This increases the flux of ballistic He incident on the MOT by a factor of 4. In this configuration we measure \( \tau_{\text{MOT}} \) to decrease by only \( \sim 20\% \), suggesting that collisions with ballistic helium are not the primary loss mechanism. With \( \phi = 20 \text{ scm} \), the reduction in the rotation speed of the turbomolecular pumps in the trapping region by a factor of 5, resulting in an increase in all background gas pressures by \( \sim 5\times \). In this configuration we measure \( \tau_{\text{MOT}} \) to decrease by only \( \sim 25\% \), indicating that collisions with background gases are not the primary loss mechanism.

**Modelling trap loss.** The measured MOT lifetime \( \tau_{\text{MOT}} = 56(4) \text{ ms} \) corresponds to a total loss rate \( 1/\tau_{\text{MOT}} = 18(1) \text{ s}^{-1} \). Choosing \( \tau_{\text{MOT}} \) with \( \tau = 1.25(3) \times \) is attributed to a shallow trapping potential relative to the MOT temperature, leading to molecules escaping the trap by simply being in the high energy tail of the Boltzmann distribution. Such escape rates depend exponentially on the ratio \( U_{\text{MOT}}/(k_B T_{\text{MOT}}) \) (ref. 37). The uncertainty in \( U_{\text{MOT}} \) results in predicted loss rates having inherently large associated errors. We have no direct method to measure \( U_{\text{MOT}} \). Instead, \( U_{\text{MOT}} \) is estimated by assuming that the spring constant \( k_r \) has a constant value all the way to the edges of the MOT light. This estimate yields \( U_{\text{MOT}}/(k_B T_{\text{MOT}}) \approx 4 \). This is likely to be an overestimate of \( U_{\text{MOT}}/(k_B T_{\text{MOT}}) \), since the MOT light intensity is smaller by a factor of \( \sim 200 \) at \( \rho = d_J/2 \text{ (trap edge)} \) versus at \( \rho = 0 \text{ (trap centre)} \).

We crudely model the trap loss using a simple Van’t Hoff–Arrhenius rate in the low damping limit \( \left( \phi/(2 \tau_{\text{mol}}) < \nu_p \right) \) (ref. 37):

\[ \frac{1}{\tau_{\text{MOT}}} = \frac{2 \nu_p}{\pi} e^{-U_{\text{MOT}}/(k_B T_{\text{MOT}})} \]  

Here we multiply the standard one-dimensional prefactor \( \nu_p/(2 \pi) \) by a factor of 4 to account for the two trap edges visited per oscillation and the two radial dimensions, we neglect loss along the deeper axial dimension. Note that the low damping condition is only marginally satisfied, so the prefactor must also be considered as only approximate. Using \( U_{\text{MOT}}/(k_B T_{\text{MOT}}) \approx 4 \), this yields an estimated loss rate of \( \log(1/\tau_{\text{MOT}}) \lesssim 0 \), an order of magnitude smaller than the measured loss rate. If \( U_{\text{MOT}} \) is instead assumed to have a smaller but realistic value, for example, consistent with a linear restoring force only out to the measured 1/e\(^2 \) radius (7 mm) of the MOT beams, then \( \tau_{\text{MOT}}/(k_B T_{\text{MOT}}) \approx 1.6 \), and \( \log(1/\tau_{\text{MOT}}) \approx 1 \) in fair agreement with the measured loss rate. Hence we believe that this mechanism can plausibly account for the loss rate observed in our experiment, although the evidence is not definitive.

31. Barry, J. F. Laser Cooling and Slowing of a Diatomic Molecule. PhD thesis (Yale Univ., 2013).
32. Barry, J. F., Shuman, E. S. & DeMille, D. A bright, slow cryogenic molecular beam source for free radicals. Phys. Chem. Chem. Phys. 13, 18936–18947 (2011).
33. Klo¨ter, B., Weber, C., Haubrich, D., Meschede, D. & Metcalf, H. Laser cooling of an indium atomic beam enabled by magnetic fields. Phys. Rev. A 77, 033402 (2008).
34. Lett, P. D. et al. Observation of atoms laser cooled below the Doppler limit. Phys. Rev. Lett. 61, 169–172 (1988).
35. Chu, S., Hollberg, L., Bjorkholm, J. E., Cable, A. & Ashkin, A. Three-dimensional viscous confinement and cooling of atoms by resonance radiation pressure. Phys. Rev. Lett. 55, 48–51 (1985).
36. Lett, P. D. et al. Optical molasses. J. Opt. Soc. Am. B 6, 2084–2107 (1989).
37. Hänggi, P., Talkner, P. & Borkovec, M. Reaction-rate theory: fifty years after Kramers. Rev. Mod. Phys. 62, 251–341 (1990).
Extended Data Figure 1 | Relevant energy levels and transitions in SrF.

a, Vibrational branching in SrF. Solid upward arrows denote transitions driven by the MOT lasers. Spontaneous decays from the $A^2\Pi_{1/2}(v' = 0)$ state (solid wavy arrows) and $A^2\Pi_{1/2}(v' = 1, 2)$ states (dashed wavy arrows) are governed by the vibrational branching fractions $b_0$, $b_1$, and $b_2$, as shown.

b, Optical addressing scheme for the SrF MOT.

c, Energy levels of the $X^2\Sigma(v = 0, N = 1)$ state versus $B$. Energy levels are labelled by their $m_F$ value with $m_F = 2$ (red lines), $m_F = 0$ (green), $m_F = -1$ (blue) and $m_F = -2$ (purple).
Extended Data Figure 2 | Slowing laser spectra. a, Scale diagram showing the frequency extent of the $L_{00}^S$, $L_{10}^S$, and $L_{21}^S$ slowing lasers (vertical red bars) relative to the four SR/HF manifolds of the $X^2\Sigma (v=0, 1, 2; N=1)$ states of SrF (horizontal black bars to right). The relative splittings of the four SR/HF levels in the $X^2\Sigma (N=1)$ state are the same to within $\pm 1\text{ MHz}$ for $v=0, 1, 2$ (ref. 31). The dashed lines mark the centres of the $N=1$ SR/HF levels for the labelled velocity, and the level structure shown corresponds to $v=0\text{ m s}^{-1}$.

b, Optimized spectral profiles of the three slowing lasers. The upper $x$ axis shows velocity for a Doppler shift equivalent to the frequency labelled on the lower $x$ axis. The $L_{00}^S$ light is modulated via a fibre EOM with $f_{\text{mod}}=3.5\text{ MHz}$. The $L_{10}^S$ and $L_{21}^S$ lasers are each modulated by passing through two bulk EOMs with resonant frequencies at $\pm 40\text{ MHz}$ and $\pm 9\text{ MHz}$.
Extended Data Figure 3 | Molecular beam longitudinal velocity. Shown are examples of slowed (grey circles) and unslowed (black squares) velocity profiles of the molecular beam detected upstream from the trapping region at $z_{\text{det}} \approx 1.076$ mm. These profiles are for the optimized slowing conditions that produce the largest MOT, as discussed in the main text.
Extended Data Figure 4 | MOT dependence on laser frequency. Shown is LIF in the trapping region versus detuning when $A_{00}$ and $A_{10}$ are varied together (top), when $A_{10}$ is varied alone (middle) and when $A_{10}$ is varied alone (bottom). As expected (and typically observed for atomic MOTs), the SrF MOT operates over a fairly narrow range of negative detuning values for the trapping lasers but requires only that the repump lasers be sufficiently near resonance. Error bars, standard error for multiple scans across each detuning range (14 scans for top and middle; 24 scans for bottom).