Sisyphus Laser Cooling of a Polyatomic Molecule

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We perform magnetically-assisted Sisyphus laser cooling of the triatomic free radical strontium monohydroxide (SrOH). This is achieved with principal optical cycling in the rotationally closed \(P(\text{N} = 1)\) branch of either the \(\tilde{X}^2\Sigma^+(000) \leftrightarrow \tilde{A}^2\Pi_{1/2}(000)\) or the \(\tilde{X}^2\Sigma^+(000) \leftrightarrow \tilde{B}^2\Sigma^+(000)\) vibronic transitions. Molecules lost into the excited vibrational states during the cooling process are repumped back through the \(\tilde{B}(000)\) state for both the \((100)\) level of the Sr-O stretching mode and the \((02^0)\) level of the bending mode. The transverse temperature of a SrOH molecular beam is reduced in one dimension by two orders of magnitude to \(\sim 700 \mu\text{K}\). This approach opens a path towards creating a variety of ultracold polyatomic molecules, including much larger ones, by means of direct laser cooling.

Compared to atoms, the additional rotational and vibrational degrees of freedom in molecules give rise to a wide variety of potential and realized scientific applications, including quantum computation,[1–3], precision measurements[4–7], and quantum simulation[8, 9]. While ultracold diatomic molecules will be extremely valuable in opening novel research frontiers, molecules with three or more atoms have unique capabilities enabled by their significantly more complicated structure[10–16]. For all molecules to achieve their full scientific potential, they must be cooled. Yet, the desired quantum complexity that molecules provide also leads to challenges for control, detection, and cooling[17]. Assembling ultracold molecules from two laser-cooled atoms has represented one solution and has created ultracold bi-alkali molecules[18–22], including filling of optical lattices with KRb[23]. There are several direct cooling techniques that together routinely cool a much wider variety of molecules into the Kelvin regime[17–24]. Intense research is ongoing to bring these cold molecules into the ultracold regime (<1 mK). Even though there has been experimental progress on control of polyatomics[25–30], opto-electrical cooling of formaldehyde is the only technique that has resulted in a trapped sub-millikelvin sample[31].

Cooling of the external motion of neutral atoms from above room temperature into the sub-millikelvin range (leading to, e.g., Bose-Einstein condensation) commonly relies on the use of velocity-dependent optical forces[32]. Laser cooling requires reasonably closed and strong optical electronic transitions, so its use for molecules has been severely limited. Recently, following initial theoretical proposals[33, 34] and proof-of-principle experimental results[35], laser cooling has been achieved for SrF[36], YO[37], and CaF[38, 39], including a magneto-optical trap for SrF[40–42]. Motivated by this progress on diatomic molecules, and building upon previous theoretical work[43], we recently demonstrated photon cycling – a crucial requirement for achieving light induced forces – with the triatomic molecule SrOH[44].

In this Letter, we report the Sisyphus laser cooling of a polyatomic molecule. The dissipative force for compressing phase-space volume is achieved by a combination of spatially varying light shifts and optical pumping into dark sub-levels, which are then remixed by a static magnetic field, as explored previously in atomic systems[45–48]. Since the magnitude of the induced friction force is directly related to the modulation depth of the dressed energy levels, the cooling process can be much more efficient than with Doppler radiation pressure forces[47, 48]. This enhancement is especially important for complex polyatomic molecules, where scattering the thousands of photons necessary for Doppler cooling becomes more challenging due to additional vibrational modes. Here, we demonstrate transverse cooling (and heating) of a SrOH beam using two different electronic transitions, study loss channels to vibrational states (including the bending mode), and highlight proposed extensions to more complex species.

Our work with SrOH uses the cryogenic buffer-gas beam (CBGB)[49], which is also used in all other experiments on laser cooling of molecules. The study of SrOH buffer-gas cooling dynamics, as well as precise measurements of its momentum transfer and inelastic cross sections with helium, were previously performed[50]. In brief, SrOH can be produced efficiently with ablation and forms an intense CBGB. Fig. 1 shows a simplified schematic diagram of the current experimental apparatus. Detailed descriptions of this apparatus have also been provided elsewhere[51]. Laser ablation of Sr(OH)₂ produces SrOH molecules that are then entrained in helium buffer gas (\(T_{\text{He}} \sim 2\) K) that flows out of the cell into a beam. He flow is 8 standard cubic centimeters per minute (scm), and the beam is extracted through a 5 mm diameter aperture. This CBGB contains \(\sim 10^9\) molecules in the first excited rotational level (\(N = 1\)) in a pulse ~5 ms long. The forward velocity of the SrOH beam is \(v_x \sim 130\) m/s and its transverse velocity spread is \(\Delta v_y \sim \pm 15\) m/s. A \(2 \times 2\) mm square aperture situated 15 cm away from the cell collimates the beam, resulting in an effective transverse temperature \(T_L \sim 50\) mK.

To laser cool, we use a photon cycling scheme that we also employed in an earlier work, as described in detail in Ref. [44]. The main photon cycling path is \(\tilde{X}^2\Sigma^+(000) \rightarrow \tilde{B}^2\Sigma^+(000)\) (611 nm) and the first vibrational repump is \(\tilde{X}^2\Sigma^+(100) \rightarrow \tilde{B}^2\Sigma^+(000)\) (631 nm), as shown in Fig. 1. (In-
The combined main and repump laser light, with diameter of $\sim 3$ mm, propagates in the $y$ direction and makes 5 round-trip passes between two mirrors before it is retroreflected back in order to create a standing wave. The molecule-laser interaction time is $t_{\text{int}} \sim 115 \mu s$. Each color ($611$ nm and $631$ nm) includes two frequency components separated by $\sim 110$ MHz to address the $P_{11}(J'' = 1.5)$ and $P_{12}(J'' = 0.5)$ lines of the spin-rotation (SR) splitting. We also study cooling using the $\tilde{X}^{2}\Sigma^{+}(000) \rightarrow \tilde{A}^{2}\Pi_{1/2}(000)$ excitation at $688$ nm as the main transition. Each SR component of the $688$ nm light is generated using separate injection-locked laser diodes seeded by external-cavity diode lasers in the Littrow configuration [52] resulting in $\sim 15$ mW per SR component in the interaction region. The $611$ nm light, as well as all of the repumping light, is generated by cw dye lasers passing through acousto-optic modulators.

The spatial profile of the molecular beam is recorded by imaging laser-induced fluorescence (LIF) in the Detection region. The molecules are excited using a transverse retroreflected laser beam and LIF photons are imaged onto an EMCCD camera. The detection laser addresses both SR components of the $P(N'' = 1)$ line for the $\tilde{X}^{2}\Sigma^{+}(000) \rightarrow \tilde{A}^{2}\Pi_{1/2}(000)$ transition, as shown in Fig. 1 (Detection). In a similar laser configuration, time of flight (ToF) data is recorded by collecting the LIF on a PMT (further downstream). In order to boost the LIF signal there is a Clean-up region where all of the molecular population is pumped into the ground state ($\tilde{X}(000)$) from the excited vibrational levels ($\tilde{X}(100)$ and $\tilde{X}(02^0)$). This is done with off-diagonal excitation to $\tilde{B}(000)$, as shown in Fig. 1 (Clean-up).

Fig. 2 shows 2D camera images of the molecular beam for various detunings of the $\tilde{X} - \tilde{A}$ cooling laser. Phase-space compression is clearly visible in the comparison between images (b), $\delta = 0$, and (d), $\delta > 0$, cooling.

To characterize the cooling efficacy for both $\tilde{X} - \tilde{A}$ and $\tilde{X} - \tilde{B}$ cycling transitions, we plot integrated 1D ($x$ axis) beam profiles for both cooling configurations in Fig. 3. The most effective laser cooling was demonstrated using $\tilde{X}(000) \rightarrow \tilde{B}(000)$
transition at 611 nm with laser intensity $I = 1.4 \text{ W/cm}^2$, resulting in a saturation parameter $s \sim 20$ (Fig. 3a). From the fits to the data and a comparison to Monte Carlo (MC) simulations of the molecular beam kinetics we determine the final beam temperature $T_B \sim 700 \mu\text{K}$, which corresponds to a factor of 70 reduction as compared to the $\delta = 0$ detuning. Because of the high damping rate, we achieve lower transverse temperature than previously demonstrated with a 1D MOT of diatomic molecules [37], with half the interaction length.

Cooling using the $\tilde{X} - \tilde{A}$ transition was less effective. Fig. 3(b) shows typical molecular beam profiles after interacting with a cooling laser exciting the $\tilde{X} - \tilde{A}$ transition at 688 nm with intensity of $I = 424 \text{ mW/cm}^2$ and a saturation parameter $s \sim 8$. For a positive detuning we observe cooling of the SrOH beam represented by the increased molecular density near the center due to the narrowing of the spatial distribution. By comparing the fitted width of the resulting profile with a MC simulation we conclude that the beam is cooled to a final temperature of $\sim 2 \text{ mK}$, an order of magnitude above the Doppler limit of $\sim 200 \mu\text{K}$.

In order to extract the number of scattered photons during the cooling process, we determine the fraction of the remaining molecules after the cooling process with ToF PMT data taken without the $(02^0)$ clean-up beam. Using the previously measured decay rate to dark vibrational levels (above $\tilde{X}(100)$) of $(3 \pm 1) \times 10^{-3}$ [44], we calculate that on average each molecule emits $220^{+110}_{-60}$ photons with a scattering rate of $\Gamma_{\text{scat}} = 2 \pm 1 \text{ MHz}$. In such a configuration, Doppler cooling from radiation-pressure molasses does not play a significant role [47]. By adding the $(02^0)$ clean-up beam, we determine that $\sim 10\%$ of molecules decay to the $(02^0)$ state of the bending mode during the cooling process.

![Figure 2](image_url)

Figure 2. Spatial images of the molecular beam taken at different detunings of the $\tilde{X}(000) - \tilde{B}(000)$ cooling laser: (b) on resonance, (c) red-detuned (-10 MHz), and (d) blue-detuned (+10 MHz). The same color axis is used for all three plots. SrOH beam is moving in the x direction while the cooling laser is applied in the y direction as shown in (a). Narrowing of the spatial size of the molecular cloud with accompanying density increase in (d) compared to (b) in the y dimension indicates phase-space compression.

For negative detunings the molecules are expelled from the region around $v_r = 0$, leading to a double-peak structure that is a signature of the magnetically-assisted Sisyphus effect [45]. Compared to the results of cycling on the $\tilde{X} - \tilde{A}$ transition (Fig. 3(b)), the use of the $\tilde{X} - \tilde{B}$ transition (Fig. 3(a)) increases the separation between the peaks from $2.95 \pm 0.04$ mm to $7.54 \pm 0.04$ mm for $\delta < 0$. Our findings are in good agreement with previous studies of sub-Doppler laser cooling in complex multilevel atomic [56] and molecular systems [36, 57].

In summary, we demonstrate Sisyphus laser cooling of the polyatomic molecule SrOH. We reduce the transverse temperature of a cryogenic buffer-gas beam from 50 mK to 700 $\mu\text{K}$ with $\sim 200$ scattered photons per molecule. Laser cooling of atoms is a mature scientific field [58–60] with well-developed experimental [61–62] and theoretical [63–64] techniques. Our results with SrOH open up a wide range of future directions for laser manipulation of polyatomic molecules. Cooling SrOH motion with magnetically-assisted laser cooling close to the recoil temperature of $\sim 1 \mu\text{K}$ should be possible by increasing the interaction time and optimizing laser power [65–66]. Extending the scheme to 2D and using more elaborate optical configurations would lead to significantly increased brightening of the molecular beam [66–67]. Slowing and cooling of an atomic beam in the longitudinal dimension [68–69], e.g. for loading into a MOT, could now be extended to polyatomic molecules.

While some of these research avenues might require repumping of other vibrational states beyond the $(100)$ and $(02^0)$ states as the number of scattered photons increases, this challenge can be solved with additional repumping lasers on the $\tilde{X} - \tilde{B}$ transition. Since the strengths of higher-order Franck-Condon factors decrease rapidly [55–70], scattering of $\sim 10,000$ photons should be possible with only two additional lasers to address $(200)$ and $(01^1)$ states. All of the required frequencies can be generated with solid-state laser diodes that have easily attainable requisite powers [71]. Moreover, by using $\tilde{X} - \tilde{A}$ electronic excitation for laser cooling and $\tilde{X} - \tilde{B}$ excitation for repumping, the scattering rate becomes independent of the number of repumping lasers, ensuring rapid optical cycling at a maximum possible rate.

While SrOH has a linear geometry in the vibronic ground state, it still serves as a useful test candidate for the feasibility of laser cooling more complex, nonlinear molecules like strontium monoalkoxide free radicals, where hydrogen is replaced by a more complex group $R$ (e.g. $R = \text{CH}_3$). Since SrOR molecules share a number of properties with SrOH, including a very ionic Sr-O bond, diagonal Franck-Condon factors, and technically accessible laser transitions [72–73], results presented in this paper could naturally be extended to such complex species [74].
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