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Ultracold polyatomic molecules for quantum science and precision measurements

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Polar molecules, due to their intrinsic electric dipole moment and their controllable complexity, are a powerful platform for precision measurement searches for physics beyond the Standard Model (BSM) and for quantum simulation/computation. This has led to many experimental efforts to cool and control molecules at the quantum level. Due to their qualitatively unique rotational and vibrational modes, polyatomic molecules (molecules containing three or more atoms) have attracted recent focus as quantum resources that have distinct advantages and challenges compared to both atoms and diatomic molecules. Here we discuss results on the laser cooling of polyatomic molecules into the ultracold regime and future prospects for the use of polyatomic molecules to greatly improve fundamental symmetry tests, searches for dark matter, and the search for CP-violating BSM physics.

KEYWORDS: ultracold molecules, optical cycling, functionalized molecules, fundamental symmetry violation, quantum science

1. Introduction

Assembled quantum systems controlled at the single-quantum-state level are the forefront systems in quantum science. Arrays of atomic ions [1–3], neutral atoms [4–7], and neutral diatomic molecules [8–11] have been created to realize viable quantum information platforms [12, 13]. These platforms allow for high-fidelity detection of single particles and provide unprecedented and scalable access to the microscopic details of interesting many-body quantum phenomena.

Molecules also have an important role to play in particle physics. Atoms and molecules brought under single internal quantum state control, even in a simple thermal ensemble, can be used for precision spectroscopy to probe for physics beyond the Standard Model (BSM). This has already been shown to be effective with diatomic molecules in the search for the electron electric dipole moment (EDM), which has broadly constrained new CP-violating physics well above the TeV mass range [14, 15]. Polyatomic molecules are predicted to be excellent probes of the fundamental symmetries of nature, including improved searches for EDMs and other BSM physics [16–18].

Optical trapping can be used to create arrays of single molecules or to simply hold the molecules for precision spectroscopy (eliminating time of flight broadening). One key features of optical traps include the possibility of confining molecules to sub-micron size scales (allowing molecules to be brought close enough to interact strongly for, e.g., quantum computation/simulation). Another is that the trapping light field can be weakly perturbing, providing for small systematic shifts in precision spectroscopy. Concomitant with these positive features, is the inherent limitation that optical trap depths are no larger than about 1 mK. Thus, implicit in their use is the need to first cool molecules to the ultracold regime ($\lesssim$ 1 mK). This temperature regime can be reached using rapid photon cycling (RPC), to provide laser cooling, where the photon cycle must be employed on the order of 10^3 times for useful cooling (see Fig. 1). To date, RPC has been demonstrated for highly symmetric atoms

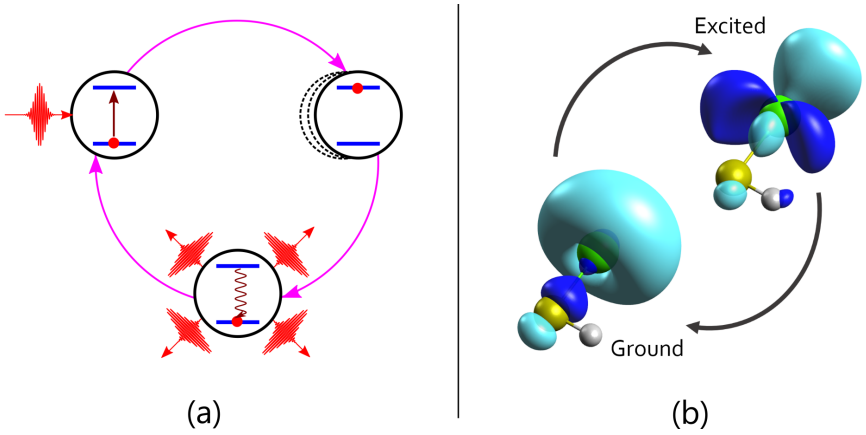

Fig. 1. (a) Schematic diagram of optical cycling in an ideal two - level system: directional photon absorption, momentum change due to photon absorption, and isotropic spontaneous emission leading to decay to the initial quantum level. Complex structures (of either atoms or molecules) can interrupt this cycle, e.g., by the addition of multiple decay pathways for spontaneous emission. (b) Molecular orbitals involved in a molecular optical cycling scheme, computed for the example of calcium hydrosulfide (CaSH). Note that the orbitals are highly localized on the atomic Ca optical cycling center, and that these orbitals somewhat resemble an atom-like *s* to *p* transition.

and molecules in which the inherent structural symmetry leads to electric dipole selection rules that aid the task of scattering approximately 10^4 photons, enough to realize laser cooling. It is important to note that RPC also enables high-fidelity quantum state preparation and read out, important for both quantum information applications and spectroscopy. So, achieving RPC provides full quantum control over both the internal and external states of the molecule, providing a near-perfect platform for a variety of quantum science endeavors.

Compared to atoms and molecules, *polyatomic* molecules (those containing three or more atoms) offer qualitatively distinct vibrational and rotational motions that enable new opportunities in physics, chemistry, and quantum technology. For instance, all polyatomic molecules have long-lived states with body-frame angular momentum arising from nuclear motion. These states offer level structures with Debye-level Stark shifts at low applied electric fields, as well as extremely field insensitive molecular orientation states, including one with near zero lab frame dipole moment. Polyatomic molecules also often possess nearly degenerate rovibrational levels with enhanced sensitivity to new physics such as ultralight bosonic dark matter [19]. However, the rich internal structure of polyatomic molecules also makes the task of laser cooling molecules appear quite challenging. In particular, the many vibrational and rotational states present in polyatomic molecules constitute a vast reservoir of potential "loss channels" that could interrupt the laser cooling process (the repeated excitation and spontaneous decay process of Fig. 1). In a typical molecule, electron excitation followed by spontaneous photon emission might cause dozens (or more) of vibrational and rotational states to become populated—– too many to feasibly control with lasers in the laboratory (at least with current laser technology).

Exciting recent results have demonstrated that RPC and laser cooling, the "workhorse" tools of atomic, molecular, and optical physics (AMO) that enable control over individual particles at the single-quantum-state level, can be extended to certain broad classes of polyatomic molecules. In this manuscript, we discuss some of this progress. First, we summarize applications in both quantum science and precision measurements that motivate this effort. Then, we explain the process of laser cooling that has been used to trap and cool both diatomic and polyatomic molecules. Finally, we provide an outlook on the scientific goals that could be achieved as RPC and laser cooling are applied to more complex and larger polyatomic molecules.

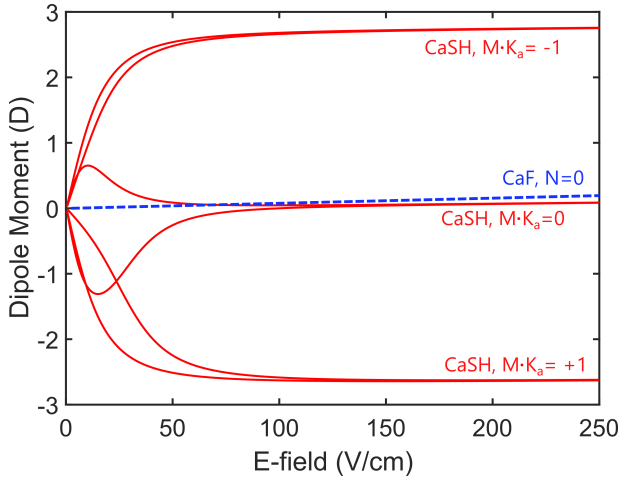

Fig. 2. Lab-frame dipole moments of CaSH $K_a = 1$ states (red solid lines) and the CaF $N = 0$ state (blue dashed line) in applied electric fields between $E = 0$ and 250 V/cm.

2. Why cold polyatomic molecules?

Unlike diatomic molecules, polyatomic molecules possess rotational and vibrational modes involving rigid body rotation about the internuclear axis The presence of rotations about the molecular symmetry axis (quantum number labeled as K for rotations and ℓ for vibrations) leads to many useful properties for applications in quantum science and precision measurement. For example, states with $K \geq 1$ (or equivalently $\ell \geq 1$) possess nearly-degenerate levels of opposite parity that can be fully polarized at fields as small as a few V/cm. An example of this structure is displayed in Fig. 2, where the calculation is performed for the bent triatomic molecule CaSH in the $K = 1$ state. A similar structure exists in linear triatomic molecules, although in that case the parity doubling is caused by (bending) vibrational angular momentum. Figure 2 compares the induced dipole moment of CaSH against a linear analog, CaF, demonstrating that while full polarization of the polyatomic molecule is possible, the diatomic molecule is much more difficult to orient in the laboratory frame.

2.1 Quantum Science Applications

Ultracold molecules with large electric dipole moments are a new platform for quantum simulation [20–25] and quantum information processing [26–30]. Polyatomic molecules such as CaOH, $CaOCH_3$, and CaSH are very well suited for these experiments due to their small parity doublets, reasonably large permanent dipole moments, and complex– but fully controllable– internal structure. Recent progress with atoms and molecules has demonstrated the power of optical tweezer arrays for quantum science experiments [12, 13, 31, 32]. In linear molecules such as CaOH, the highly polarizable state comes from a vibrational bending mode with spontaneous lifetime $\tau \sim 750$ ms. Although this time is ample for a whole swath of frontier quantum science research, using a species with longer lifetime may be an advantage. The polarizable states in either $CaOCH_3$ or CaSH arise from rotational angular momentum and have lifetimes $\gg 10$ s, which is very promising for maintaining coherence over an entire array of individually trapped molecules for the timescales required to implement many thousands of gate operations.

The complex internal structure of asymmetric top molecules (ATMs) also allows robust encoding of quantum information, as recently proposed by the Preskill group in Ref. [33]. Additionally, the rich internal structure of polyatomic molecules will allow robust implementation of qudits, higher dimensional analogs of two-level qubits [34]. This could enable improved error correction [35–38], larger Hilbert spaces with fewer physical particles, and faster computation times.

2.2 Precision Measurements

Polyatomic molecules provide new opportunities for performing precision spectroscopy in order to test the Standard Model of particle physics (SM) and to discover new physical phenomena beyond the scope of the SM description (e.g. SUSY, Lorentz invariance violation) [18, 39, 40].

Searching for Time Variation of Fundamental Constants In certain beyond-SM theories, fundamental constants such as the proton-to-electron mass ratio, μ, are expected to change over time. Generically, molecular energies involving vibration and rotation depend directly on μ. Some transitions with orders-of-magnitude increased sensitivity to changes in μ— such as those involving torsional, hindered rotational, and nuclear tunneling motions, as well as those involving two or more distinct vibrational modes— are only present in polyatomic molecules [41]. Monitoring changes in the resonance frequency of such transitions over time therefore enables more precise tests varying fundamental constants.

To date, the highest-precision laboratory measurement of μ variation in a molecule was performed in an ultracold KRb [42], while the most stringent limits on a linear drift in μ are obtained from torsion-rotation transitions in methanol [43]. Ultracold polyatomic molecules may reach even higher sensitivity owing to their combination of laser-coolability and rich vibrational structure. For example, the energies of two nearly-degenerate vibrational states in SrOH depend differently on μ, so that the fractional change in the resonance frequency of a microwave transition between them would be 10^3 times larger than any fractional change in μ [19]. Owing to the long coherence times of trapped, ultracold molecules, precision spectroscopy of this transition could probe new physics that would cause temporal variation of μ.

Testing Quantum Statistics Testing violations of the Pauli principle and the indistinguishability of identical particles is another area of fundamental physics where spectroscopy of polyatomic molecules has made fruitful contributions. Spectroscopy of molecules with two or more identical nuclei can place limits on the degree of quantum statistics violations, testing theory [44]. Spectroscopy of $^{12}C^{16}O_2$ shows that fewer than 1 in 10^{11} such molecules have ^{16}O nuclei whose wave functions are antisymmetric under exchange [45], validating the spin-statistics connection. Violations of an often-linked, but distinct, principle known as the symmetrization postulate would allow more complicated symmetries under particle exchange, and can only be tested in systems with more than two indistinguishable particles [46]. Precision spectroscopy of polyatomic molecules with at least three identical atoms have been proposed to test this assumption of quantum mechanics [47, 48].

Search for New Physics, High Mass Particles Molecular spectroscopy can provide information about possible CP violating fundamental particles with masses beyond the reach of the LHC [39, 49]. Polar diatomic molecules are currently used to search for the permanent electric dipole moment (EDM) of the electron, which can signal the presence of new particles in the TeV range, and associated time-reversal symmetry breaking [14, 15]. In diatomic molecular EDM experiments, the required states that can be easily polarized are frequently metastable (with short lifetimes around 5 ms, like in ThO), and photon cycling and laser cooling is prevented by the particular energy level structure of those states. Polyatomic molecules could potentially solve both of these challenges. For example, linear triatomic molecules in long-lived excited bending vibrational states that can be easily polarized with small laboratory fields could potentially enable very large sensitivity enhancements in EDM experiments while also being laser-coolable [16, 50]. YbOH has recently been laser-cooled [51] based on these motivations. A symmetric top variant ($YbOCH_3$) has also been proposed for probing PeV-scale new T-violating physics [16, 17], thus further motivating the exploration of laser cooling and trapping for non-linear molecules.

Finally, precision spectroscopy of laser-cooled polyatomic molecules can test predictions of the Standard Model and improve benchmarking of theory in systems where exact calculations cannot be performed [52]. A wide variety of molecules has been proposed for measuring nuclear-spin-dependent parity violation, which can arise from the Standard Model weak interaction. These species

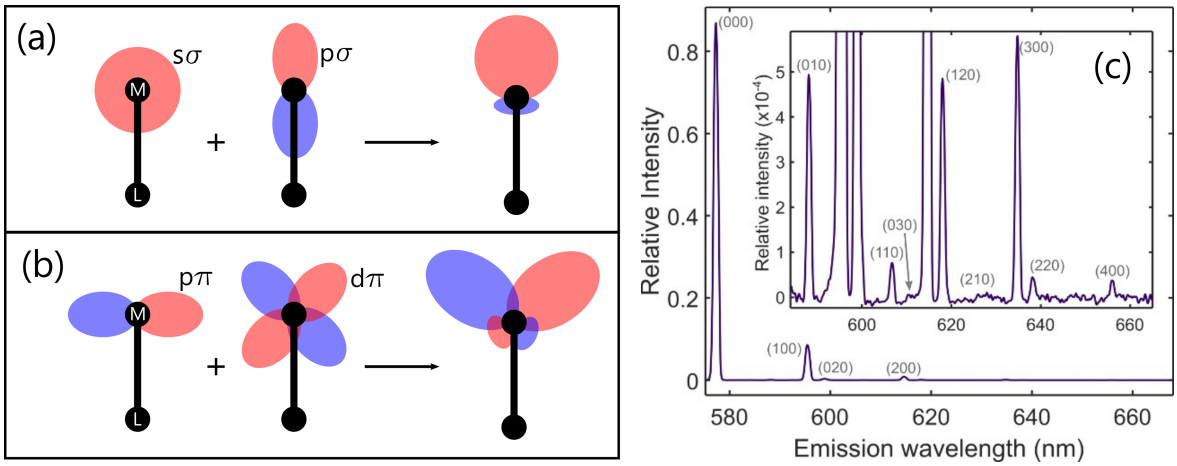

Fig. 3. Illustration of orbital mixing between (a) $s\sigma$ and $p\sigma$ orbitals to generate a $\tilde{X}\,^2\Sigma^+$ state and (b) $p\pi$ and $d\pi$ orbitals to generate the a $\tilde{A}\,^2\Pi$ state. In both cases, the rightmost image shows quantum chemical calculations of the electronic distribution confirming this simple orbital mixing picture. (c) Experimental DLIF trace recorded for YbOH molecules following excitation to the $\tilde{A}\,^2\Pi_{1/2}(v = 0, J = 1/2, p = +)$ level. Inset shows the detail near the baseline, demonstrating that relative intensity sensitivity around 10^{-5} is achieved. Labels above each peak indicate the ground state vibrational level that the decay populates.

span the relatively light and simple molecule BeNC, for which the relevant nuclear and molecular calculations are tractable, to RaOH, which remains out of reach for highly precise calculations. As with many of the previous examples, laser cooling promises many orders of magnitude higher sensitivity by providing increased coherence times, as well as improved control of potential systematic errors.

3. Identifying and Producing Laser-Coolable Molecules

Among the numerous molecules that may be useful for the applications outlined above, our group has focused on a broad class of molecules that are amenable to photon cycling and, by extension, laser cooling. Laser cooling relies on photon cycling to generate dissipative forces. Typically, about 10^4 photon scatters are necessary to apply sufficient force for slowing a molecular beam, capturing molecules into a magneto-optical trap, and cooling them to below the Doppler limit. Note that laser slowing is arguably the most difficult of these steps, and requires the largest number of photon scatters. For this reason, alternative slowing methods that rely on fewer photon scatters have been widely pursued [53, 54].

Achieving these steps requires an excited state that decays preferentially to one ground state, with unplugged leaks to all other (possibly metastable) levels below about 1 part in 10^4. The simplest atoms with this electronic structure are alkali metal atoms with low-lying $^2S \rightarrow {}^2P$ transitions (the $D1$ and $D2$ lines). In the case of molecules, certain classes with $^2\Sigma^+$ ground states have been found to be favorable to laser cooling due to their single valence electron in a metal-centered $s\sigma$ orbital [55, 56]. These species can be thought of as the molecular analogs of alkali atoms in the sense that they have a single optically active electron with essentially "atom-like" transitions, see Fig. 3(a).

Electronic closure can be ensured by exciting to low-lying electronically excited states that have no levels between them and the absolute ground state. Each time a molecule is excited and spontaneously emits a photon, it is still possible that the vibrational and/or rotational state will change. Fortunately, closed rotational cycling schemes can be found for essentially all molecular structures of interest, relying on a combination of parity and angular momentum selection rules [56–58].

Even without any electronic or rotational loss channels, the absence of angular momentum associated with the stretching modes of vibrational motion will lead to losses to excited vibrational levels.

Vibrational losses are strongly suppressed in molecules for which the ground- and excited-state potential energy surfaces resemble one another, as they do for alkaline-earth metal atoms monovalently and ionically bonded to an electronegative ligand (CaF, CaOH, $CaOCH_3$, etc.). As shown in Fig. 3(a), electrostatic repulsion between the metal-centered valence electron and the negatively charged ligand leads to orbital hybridization that excludes valence electron density from the bonding region and thus decoupling between electronic and vibrational excitations [55]. Importantly, this bonding behavior remains true regardless of the alkaline-earth (or alkaline-earth-like) metal atom chosen (e.g., M = Ca, Sr, Ba, Yb) and for a wide range of electronegative ligands (e.g., -OH, $-OCH_3$, -SH, $-NH_2$, etc.).

The intensities of vibronic transitions are governed not by strict selection rules, but by the values of so-called Franck-Condon factors (FCFs) which characterize the overlap between ground and excited vibrational wave functions. The possible decay pathways and their relative strengths can be experimentally measured by driving molecules to a particular excited state and measuring the relative intensities of the various wavelengths at which spontaneous emission occurs, e.g. using dispersed laser-induced fluorescence (DLIF). The pioneering use of DLIF measeurements to identify laser coolable molecules were carried out by the Steimle group [59–61]. Recently, we have improved the intensity senstivity achievable in these measurements to about 10^{-5}, allowing us to characterize all loss channels that must be repumped for a full cooling and trapping experiment [62]. Figure 3(c) shows a measurement determining the FCFs for the $\tilde{X} - \tilde{A}$ band of YbOH [62]. Because of the highly diagonal FCFs, fewer than a dozen vibrational decay channels need to be repumped to ensure "closure" to the level of 1 part in 10^5. These highly diagonal FCFs are characteristic of a large class of molecules comprised of alkaline-earth atoms ionically bonded to halogen-like ligands, as was originally noted by Di Rosa [56].

Because laser-coolable molecules typically have unpaired valence electrons (which give them laser-accessible electronic transitions), they are chemically unstable and cannot be obtained from a "bottle." Instead, we generally produce these molecules by laser ablation of a stable precursor, possibly in the presence of a reagent gas. Once produced, the molecules must be "pre-cooled" in order to achieve a significant population in any single quantum state (including rotational, vibrational, and electronic degrees of freedom). In all molecular laser cooling experiments to date, this has been done by collisionally cooling with a cold, inert buffer gas ("buffer gas cooling") to temperatures of 1-4 K. The relatively low resulting molecular velocities, ∼100 m/s, also allow for laser cooling and trapping with a practically achievable number of scattered photons.

The molecules produced as described above still move too quickly to be directly captured in a magneto-optical trap (MOT). Molecules are next slowed down to ∼10 m/s by subjecting them to the radiation pressure force of counter-propagating laser beams [63]. These molecules can then be loaded into a MOT and quickly cooled to the Doppler limit, and finally sub-Doppler cooled to temperatures of ∼5 μK [64, 65]. Finally, molecules can be loaded into a conservative trap of choice, either optical [9, 66] or magnetic [67, 68].

4. Experimental Progress

4.1 Linear Triatomic Molecules

The first polyatomic molecule to be directly laser cooled was SrOH [69]. In these transverse cooling experiments, the transverse temperature of a SrOH molecular beam was reduced from 50 mK to 750 μK in one dimension using only 220 scattered photons per molecule. To apply the cooling forces on the collimated SrOH molecular beam, we used transverse lasers retro-reflected between two mirrors in order to generate a standing wave. Depending on the experimental configuration, either the $\tilde{X}^2\Sigma^+(000) \rightarrow \tilde{A}^2\Pi_{1/2}(000)$ or the $\tilde{X}^2\Sigma^+(000) \rightarrow \tilde{B}^2\Sigma^+(000)$ cooling transition is used with an additional $\tilde{X}^2\Sigma^+(100) \rightarrow \tilde{B}^2\Sigma^+(000)$ laser for repumping molecules decaying to the vibrationally excited Sr-O stretching mode. In order to remix dark magnetic sub-levels, a magnetic field is applied

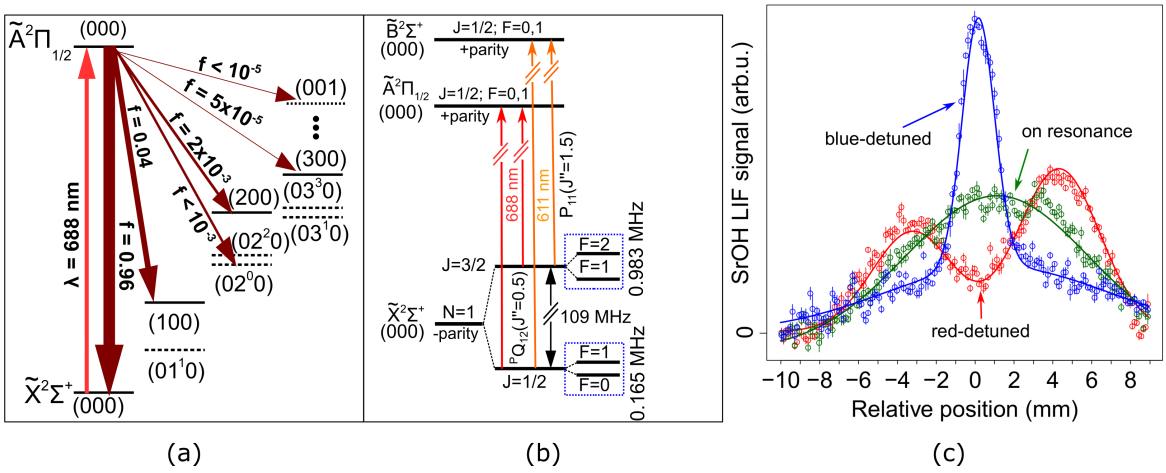

Fig. 4. Laser cooling of the SrOH molecule. (a) Vibrational branching ratios relevant for the SrOH $\tilde{A}\,^2\Pi_{1/2}$ state. In the experiment, the (100) and (02^0) levels were repumepd. (b) Rotational substructure of each vibronic band pumped. Two spin-rotation features are addressed. Either the $\tilde{A}$ or $\tilde{B}$ state is targeted for laser cooling. (c) Transverse laser cooling of an SrOH molecular beam from 50 mK (green curve) to 750 μK (blue curve). The dramatic reduction of transverse spatial extent is indicative of cooling. Also shown (red curve) is the effect of laser heating, increases the molecular velocities in the transverse direction and therefore causes accumulation off of the molecular beam axis.

at an angle relative to laser polarization in the interaction region. Before the detection is performed, molecules remaining in either (100) or $\left(02^00\right)$ excited vibrational levels of the electronic ground state are optically pumped back into the ground vibrational level using $\tilde{X} \rightarrow \tilde{B}$ off-diagonal excitations. The spatial profile of the molecular beam is imaged on an electron multiplying charge-coupled device (EMCCD) camera and the time-of-flight (TOF) data is collected on a photomultiplier tube (PMT). Figure 4 demonstrates the results of both Sisyphus laser heating and cooling of the cryogenic beam.

Following the original work on SrOH, the molecules YbOH and CaOH were both laser cooled in one dimension. For YbOH, which is of interest to search for *CP*-violating electromagnetic moments, both Sisyphus and Doppler cooling were observed [51]. The transverse temperature of the YbOH beam was reduced from about 20 mK to below 600 μK while scattering approximately 500 photons. For CaOH molecules, a one-dimensional magneto-optical trap was realized and similarly low temperatures were achieved [71].

Very recently, the linear triatomic molecule CaOH has been loaded into a 3D MOT and cooled below the Doppler limit [72]. This was achieved by optically repumping 11 vibrational and rotational loss channels identified from DLIF measurements [62], enabling an average of 12000 photon scatters per molecule before loss to rovibronic dark states occured. The repumping scheme employed is illustrated in Fig. 5. A buffer gas-cooled beam of CaOH was radiatively slowed from a peak velocity of 140 m/s to <10 m/s by scattering photons on the $\tilde{X}^2\Sigma^+$ (000) $\rightarrow$ $\tilde{A}^2\Pi_{1/2}$ (000) transition at 626nm. A radio-frequency MOT [73] was then realized on the same $\tilde{X} \rightarrow \tilde{A}$ transition, allowing $\sim$ 20000 CaOH molecules to be captured and cooled to below 1 mK (Fig. 3(b)). After the MOT was formed, an optical molasses was applied to cool the CaOH molecules to 110 μK – below the Doppler cooling limit (Fig. 3(c)) – using the same sub-Doppler cooling techniques demonstrated previously with diatomic molecules [66, 70]. Notably, well under 1000 photons were required for the sub-Doppler cooling, indicating that such techniques remain efficient for trapped polyatomic molecules.

4.2 Nonlinear Molecules

Symmetric top molecules represent a natural next step in the "symmetry descent" from linear molecules. These molecules introduce rotational modes with angular momentum about the inter-

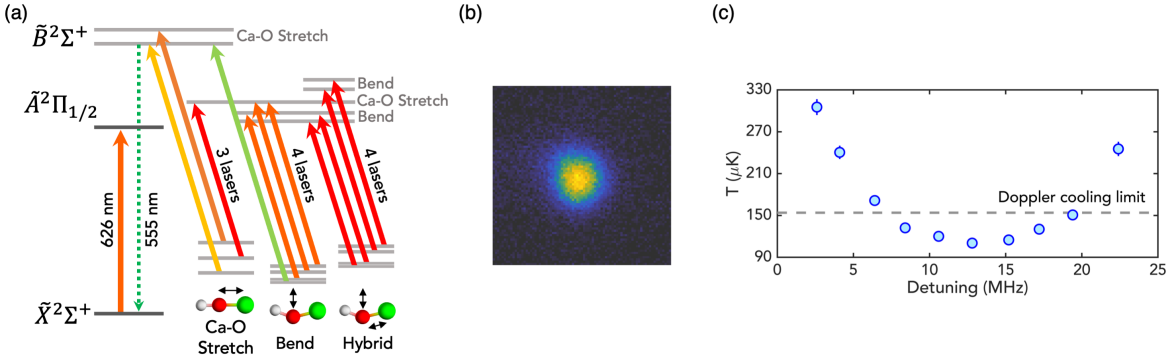

Fig. 5. Magneto-optical trapping and sub-Doppler cooling of CaOH. (a) 12 cooling and repumping lasers were used to cycle 12,000 photons per CaOH molecule, on average, before loss to dark states occurred. This photon cycling scheme was used to radiatively slow, trap, and cool CaOH. (b) Image of the CaOH MOT, containing ~20,000 molecules at temperatures of 870 μK. (c) Sub-Doppler cooling of CaOH. Scanning the detuning of the cooling light enabled the temperature of the CaOH molecular cloud to be brought below the Doppler cooling limit. Figure modified from Ref. [72].

nuclear axis ($K > 0$ states), but can be chosen to preserve many of the selection rules that were relied upon to construct closed optical cycling transitions [61, 74]. We have explored the laser cooling of these nonlinear molecules beginning with the species $CaOCH_3$. In particular, it was found that by choosing rotational states with zero angular momentum about the internuclear axis – states with quantum number $K = 0$ – the rotational photon cycling behaved equivalently to that of linear triatomic molecules. We additionally showed that photon cycling is possible in states with on-axis angular momentum, by choosing $K = 1$. This qualitatively distinct approach to photon cycling firmly demonstrated that laser cooling is feasible even for the rotational structures available in nonlinear molecules. By addressing only three vibrational levels of the symmetric top molecule $CaOCH_3$, we demonstrated 1D Sisyphus cooling of a nonlinear molecule, cooling the beam to approximately 1 mK transverse temperature (see Fig. 6) [75].

Extending the number of photons scattered to a few thousand photons appears possible with the use of around a dozen vibrational repumping lasers. When combined with "few-photon" slowing methods such as Zeeman-Sisyphus deceleration [54], magneto-optical trapping of $CaOCH_3$ appears to be a feasible goal. As with the monohydroxide series, $CaOCH_3$ is one member of a larger class of monomethoxides that appear favorable for laser cooling and trapping.

5. Toward more complex polyatomic molecules

5.1 Asymmetric Top Molecules

Additional molecular complexity can arise in a number of ways, including species with lower structural symmetry (e.g., molecules that are bent in some way) or species that contain more constituent atoms. Both cases can give rise to asymmetric top molecules (ATMs), species for which all three principal moments of inertia are different. ATMs lack the symmetries that led to certain selection rules that aided the photon cycling process for linear and symmetric top molecules, but nonetheless our group has shown theoretically that they can be controlled using slight modifications to the standard techniques [57]. In fact, we have found that an extremely broad group of molecules is amenable to these photon cycling techniques, including the structures shown in Fig. 7(i-vii).

Ultracold ATMs would offer several distinct qualitative features useful for a broad range of science. For example, ATMs generally have three permanent dipole moments that could be controlled independently, a feature not present in higher symmetry species. Furthermore, low-lying states with very long radiative lifetimes and large dipole moments promise strong molecule-molecule coupling

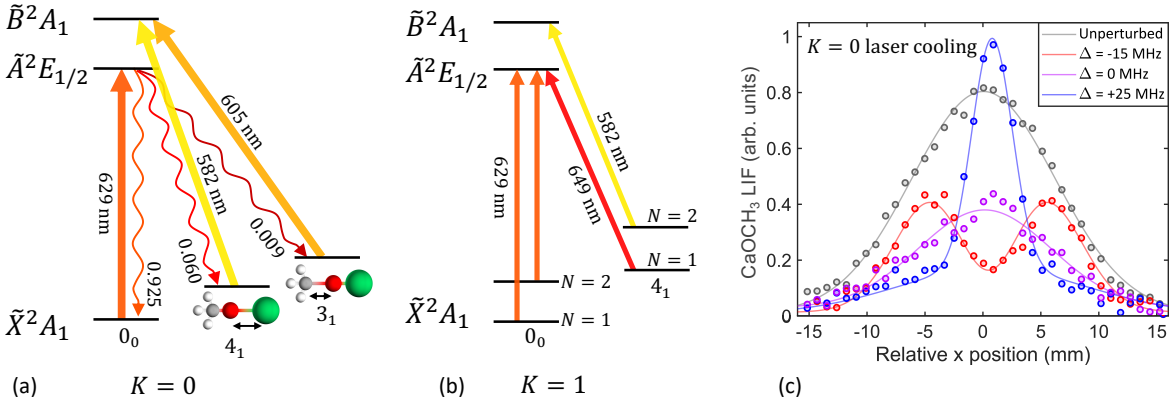

Fig. 6. Laser cooling of the symmetric top molecule $CaOCH_3$. Photon cycling schemes used to cool $CaOCH_3$ in states with (a) $K = 0$ and (b) $K = 1$, which correspond to two rotational structures also encountered in ATMs. (c) Integrated molecular beam density after Sisyphus laser cooling and heating. Laser cooling manifests itself as a narrowing of the distribution (blue), while heating is shown by expulsion of density from the central axis (red). Figure modified from Ref. [75].

in quantum simulation schemes, potentially enabling quantum gates at least an order of magnitude faster than could be achieved with laser-coolable diatomic molecules. Because the parity-doubled states come from rotational motions with typical energies $0.1 - 1$ cm^{-1} above the ground state, these useful "science" states have lifetimes orders of magnitude longer than those present in the bending vibrational modes of linear polyatomic molecules. This enhances the feasible coherence time for both precision measurement and quantum science applications to many tens of seconds.

5.2 Functionalized Aromatic Molecules

The laser cooling and full quantum control of larger molecules (containing a dozen or more atoms) is at the very frontier of the the field, so much so that ideas of what to do with them are just beginning to be explored. Fundamentally, the larger number of atoms in the molecule, the larger the number of vibrational modes and hyperfine states. The concept of "internal motion" also starts to enter, e.g. a spinning ligand. Such modes can naturally be used to store quantum information, but exactly how this can be done and how useful this will be has not been fully explored. With a large enough molecule, one may be able to completely separate the laser cooling and readout section of the molecule (through an "optical cycling center") from the physics end, perhaps containing an exotic atom such as a heavy radioactive species. Thus, one might be able to realize a "configurable" molecular framework that allows targeted substitution of scientifically interesting components.

For example, consider molecules built around aromatic rings such as benzene or naphthalene [76–78]. One can imagine functionalizing these organic precursors with a CaO bond that acts as a localized optical cycling center. By addressing the optical cycling transition between molecular orbitals localized on the Ca atom, one can feasibly cool and control the entire molecular structure. Given that the optical cycling center and the ligand functions can be made to act "orthogonally," it is clear that this structural motif leads to a highly versatile experimental platform. Indeed, the relative independence of the optically active electron from the structure of the ligand can be experimentally verified [79], as seen in the spectra of Fig. 7(a-c) [80]. The aromatic ring possesses numerous other sites that could be used to place other functional groups, e.g. high-Z nuclei for electron EDM experiments, methyl groups that introduce torsional modes with high sensitivity to μ-variation, or ^{13}C atoms for use as naturally coupled nuclear qubits. Exploring applications of large molecules, and the methods of control to bring all degrees of freedom to ultracold temperatures [81], are promising and active lines of research.

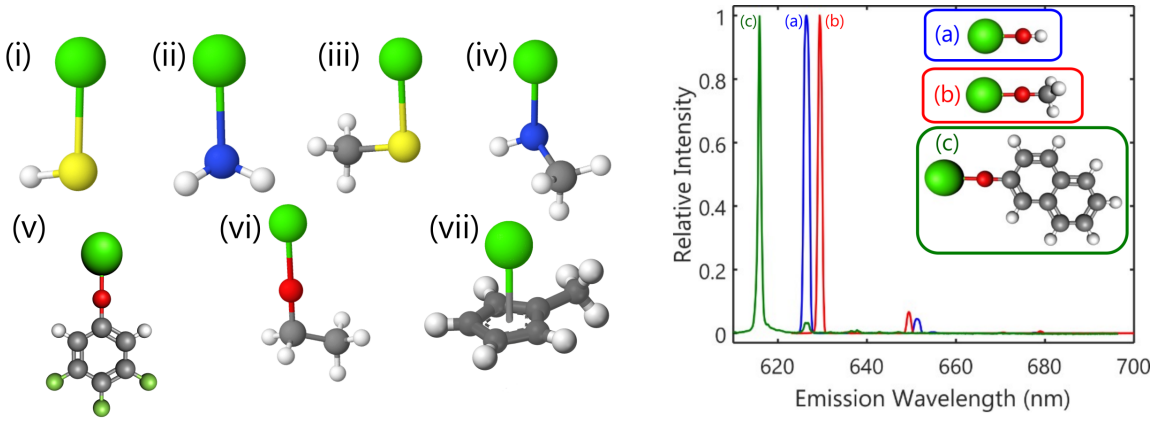

Fig. 7. (Left) Classes of asymmetric top molecules that appear amenable to photon cycling and laser cooling include: (i) MSH, (ii) MNH_2, (iii) $MSCH_3$, (iv) $MNHCH_3$, (v) MOC_6H_5 [including substitutions around the carbon ring], (vi) MOC_2H_5, and (vii) $MC_5H_4CH_3$, where M is an alkaline-earth metal atom. (Right) Comparison of DLIF spectra recorded for (a) CaOH, (b) $CaOCH_3$, and (c) $CaOC_{10}H_7$. The behavior of Ca as an optical cycling center is clearly demonstrated by the fact that the number of vibrational-state-changing decays increases only slightly as the number of vibrational modes increases by over an order of magnitude.

6. Conclusion

In summary, the field of ultracold polyatomic molecules is poised to impact many of the frontiers in modern atomic, molecular, and optical physics. Recent experimental results have shown that much of the toolbox developed for ultracold atoms can be applied to molecules with equal success. The breadth of molecular species and structures that appear amenable to laser cooling is extremely large, and continues to grow as researchers explore increasingly complex systems.

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