Laser Cooling Symmetric and Asymmetric Top Molecules

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Magneto-Optical Trapping

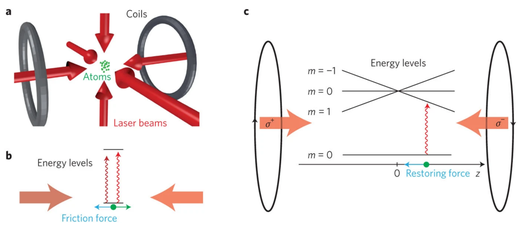

Fig. 1: Schematic for MOT

MOT is achieved by applying a magnetic field with spatial variation (generates a force proportional to the deviation from spatial origin) and a set of slowing lasers (generates a force proportional to the speed of particles).

Laser Cooling Techniques

Laser cooling relies on repeatedly scattering photons from an atom or molecule via rapid optical cycling , removing energy and entropy with directed momentum kicks and spontaneous emission events. [1]

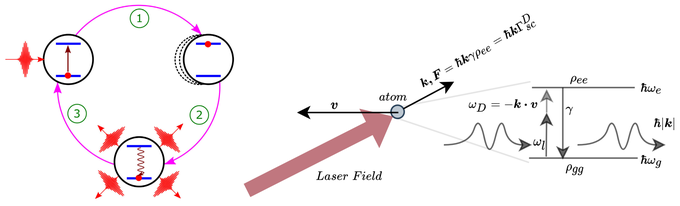

Fig. 2: **a**.Schematic diagram of optical cycling in and ideal two-level system.[4] **b**.Schematic diagram for laser cooling

Molecular Structure and Cooling

- Polyatomic molecule states if harnessed are predicted to be useful for research in quantum simulation and computation, precision measurement, ultra-cold collisions and beyond-the-standard-model searches.[1, 2]

Fig. 3: Molecular degrees of freedom and (reduced) symmetry[5]

- Consequences of reduced symmetry:
  1. Vibrational and rotational degrees of freedom lead to branching in electronic states. These states become 'dark states' when they are not coupled to the cooling laser thus the number of lasers required is impractical.
  2. Vibrational branching is governed by Franck-Condon factors(FCFs), which are not rigorous selection rules but characterization of wave function overlap between excited and ground vibrational wave functions.
  3. Rotational selection rules are still present but more complicated.
- Key ingredients/recipe for laser cooling:
  1. Strong electronic transitions between two fully bounded molecular states
  2. Diagonal FCFs, limiting branching to excited vibrational levels
  3. Rotationally closed transitions

CaOH – MOT and Cooling[2]

- Polyatomic molecules cooled and trapped in a MOT for the **first** time
- CaOH main laser cooling transition: $\tilde{A}^2\Pi_{1/2}(J' = 1/2, p' = +) \leftarrow \tilde{X}^2\Sigma^+(N'' = 1, p'' = -)$, 626 nm. $\tilde{A}^2\Pi_{1/2}$ state of CaOH is highly diagonal.

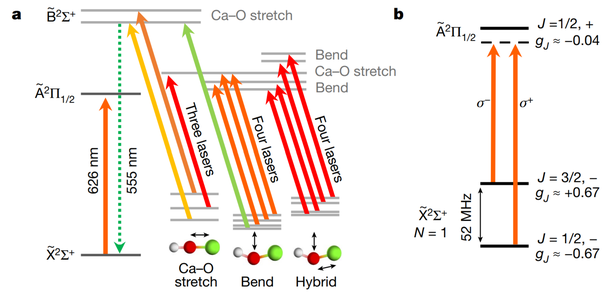

Fig. 4: **a**, CaOH transitions. **b**, CaOH MOT polarization configuration.

- Procedure:
  1. As CaOH travel to MOT region, they are illuminated with counter-propagating slowing lasers including the 'main' 626 nm transition. Additional 'repumping' lasers copropagate with main cycling light and repump population that decays to the modes in (Fig. 3a).
  2. The optical cycle for trapping CaOH: $\tilde{X}^2\Sigma^+(N'' = 1, J'' = 1/2, p'' = -)$and $\tilde{X}^2\Sigma^+(N'' = 1, J'' = 3/2, p'' = -)$components (where J is the total angular momentum) of the electronic ground state, 52MHz apart (Fig. 3b).
  3. Subsequent sub-Doppler cooling to 110(4) μK.

Symmetric Top Molecule $CaOCH_3$[1]

Fig. 5 **A** and **D** show two optical cycling schemes, which target molecules differing in their angular momentum quantum number K and their nuclear spin statistics.
In **B** and **C** We see three different vibrational levels $0_o, 4_1$ and 3_1 Total parity of each state is indicated by + and − signs.
In **E** and **F** For para-$CaCOCH_3$ the 0_o and 4_1 vibrational levels of the $\tilde{X}(K'' = 1)$ electronic ground state, driving transitions from $N'' = 1$ and $N'' = 2$ to achieve rotational closure. Each J state contains an unresolved parity doublet denoted by ±

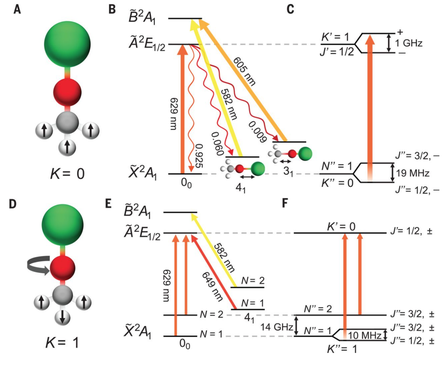

Fig. 5: $CaOCH_3$ molecule transitions

Laser Cooling Asymmetric Top Molecules(ATM)[4]

- ATM: All three principal axes have distinct moments of inertia
- Candidate species of form M-L: alkaline-earth atom(M=Mg, Ca, Sr or Ba) ionically and monovalently bonded to an electronegative ligand(L). The metal-centered unpaired valence electron is repulsed by the ligand, moved away from bond and decouples electronic and vibrational excitations.

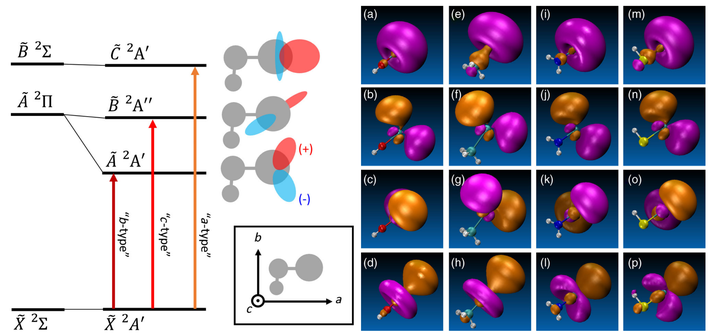

Fig. 6: **a** Representative energy-level diagram. **b**CaOH $(a-d)$ $CaCH_3$ $(e-h)$ $CaNH_2$ $(i-l)$, and CaSH$(m-p)$ [5]

- The breaking of cylindrical symmetry lifts the orbital degeneracy and the $\tilde{A}^2\Pi$ splits into two

	ΔK_a	ΔK_c	Exceptions
a type	0	±1	$\Delta N \neq 0$ for $K'_a \rightarrow K''_a = 0$
b type	±1	±1	
c type	±1	0	$\Delta N \neq 0$ for $K'_c \rightarrow K''_c = 0$

Fig. 7: Selection rules. The transition types are denoted by the dipole moment component.

Conclusion and Considerations for Further Research

- The authors argue that Born-Oppenheimer approximation will break down in some cases but this result is not detrimental to photon cycling and laser cooling as the branching introduced is contained within a small number of modes that can be easily re-pumped[5]. Our hypothesis is that further work can be done to correct the theoretical approximation by experimental data such as scaling factors.
- All the molecules, that have been cooled or theoretically considered, have specific structures, namely – that one valence electron is decoupled from the chemical bond. More calculations need to be done to (1) expand the pool of candidate molecules for laser cooling; (2) evaluate to what extent the cold molecules of proposed form could be useful.

References

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[4] Augenbraun, B. L., Doyle, J. M., Zelevinsky, T., Kozyryev, I. (2020). Molecular asymmetry and optical cycling: laser cooling asymmetric top molecules. Physical Review X, 10(3), 031022.

[5] https://chem.libretexts.org/Courses/University_of_California_Davis/UCD_Chem_110%3A_Physical_Chemistry_II/Text/12%3A_Group_Theory_-_Exploiting_Symmetry/12.2%3A_The_Symmetry_of_Molecules