

LASER COOLING SYMMETRIC AND ASYMMETRIC TOP MOLECULES

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Magneto-Optical Trapping

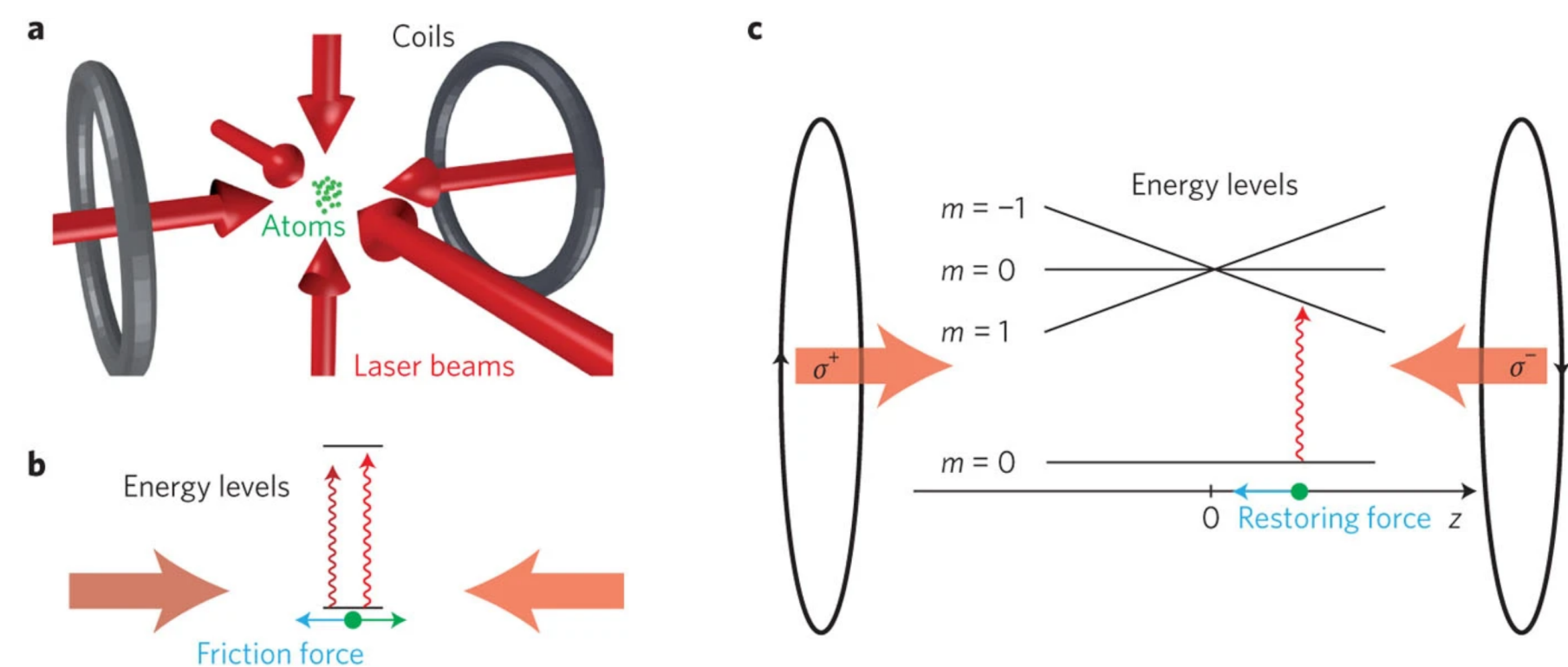


Fig. 1: Schematic for MOT

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]

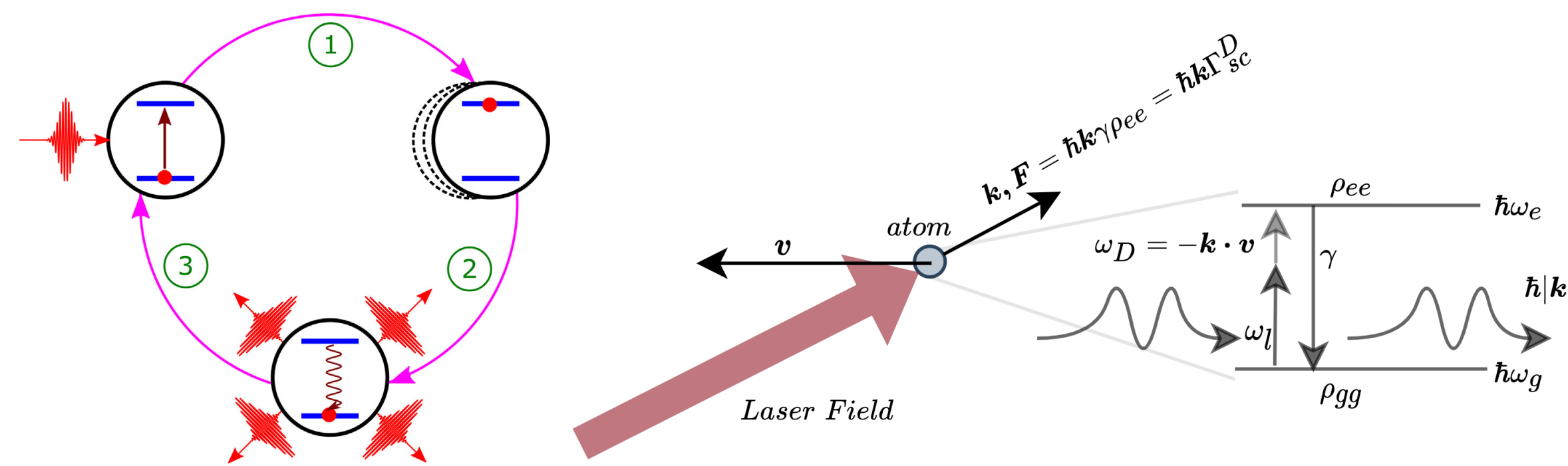


Fig. 2: **a**.Schematic diagram of optical cycling in and ideal two-level system.[4] **b**.Schematic diagram for laser cooling

Molecular Structure and Cooling

- Potentials: quantum simulation and computation, precision measurement, ultra-cold collisions and beyond-the-standard-model searches.[1, 2]

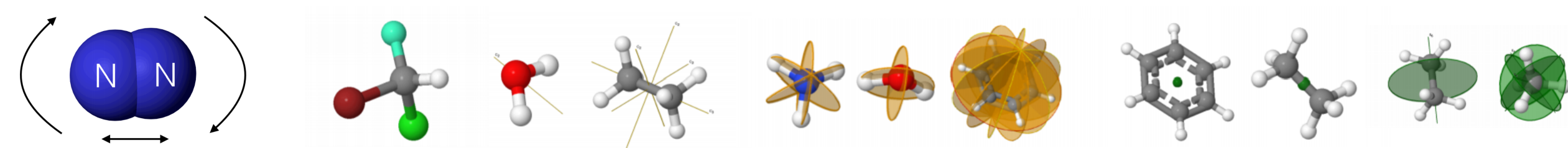


Fig. 3: Molecular degrees of freedom and (reduced) symmetry[5]

- Consequences of reduced symmetry:
 1. Additional 'dark states' not coupled to the cooling laser.
 2. Vibrational branching governed by Franck-Condon factors(FCFs). They aren't 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

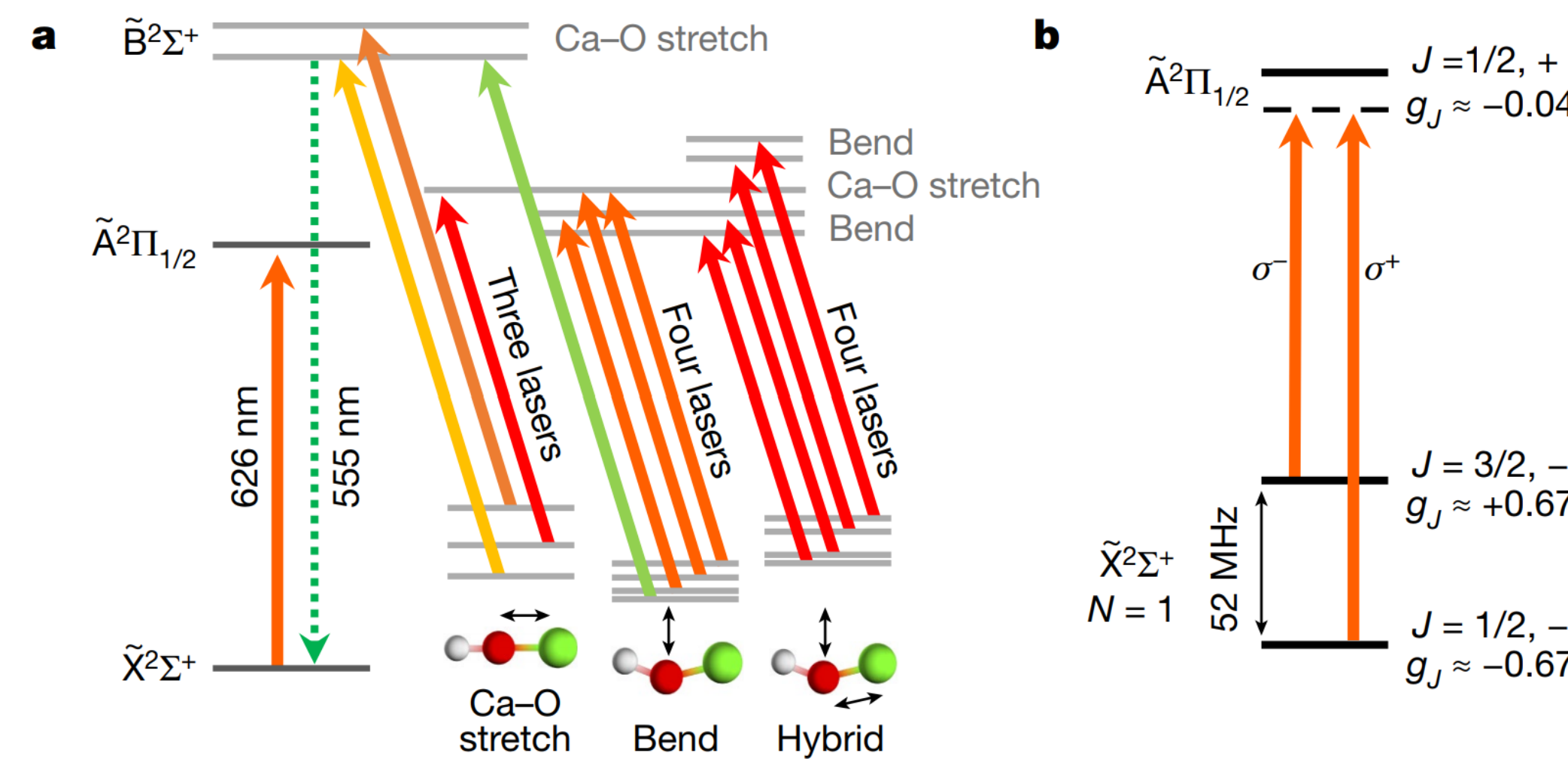


Fig. 4: **a**, CaOH transitions. 626 nm main transition. **b**, CaOH MOT polarization configuration.

- Procedure:
 1. CaOH 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) μ K.

Symmetric Top Molecule CaOCH₃[1]

Fig. 5 **A** and **D** Show two optical cycling schemes. Target molecules differing in angular momentum quantum number K and nuclear spin statistics. In **B** and **C** Show three different vibrational levels 0₀, 4₁ and 3₁ Total parity of each state is indicated by + and – signs. In **E** and **F** Show 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 \pm

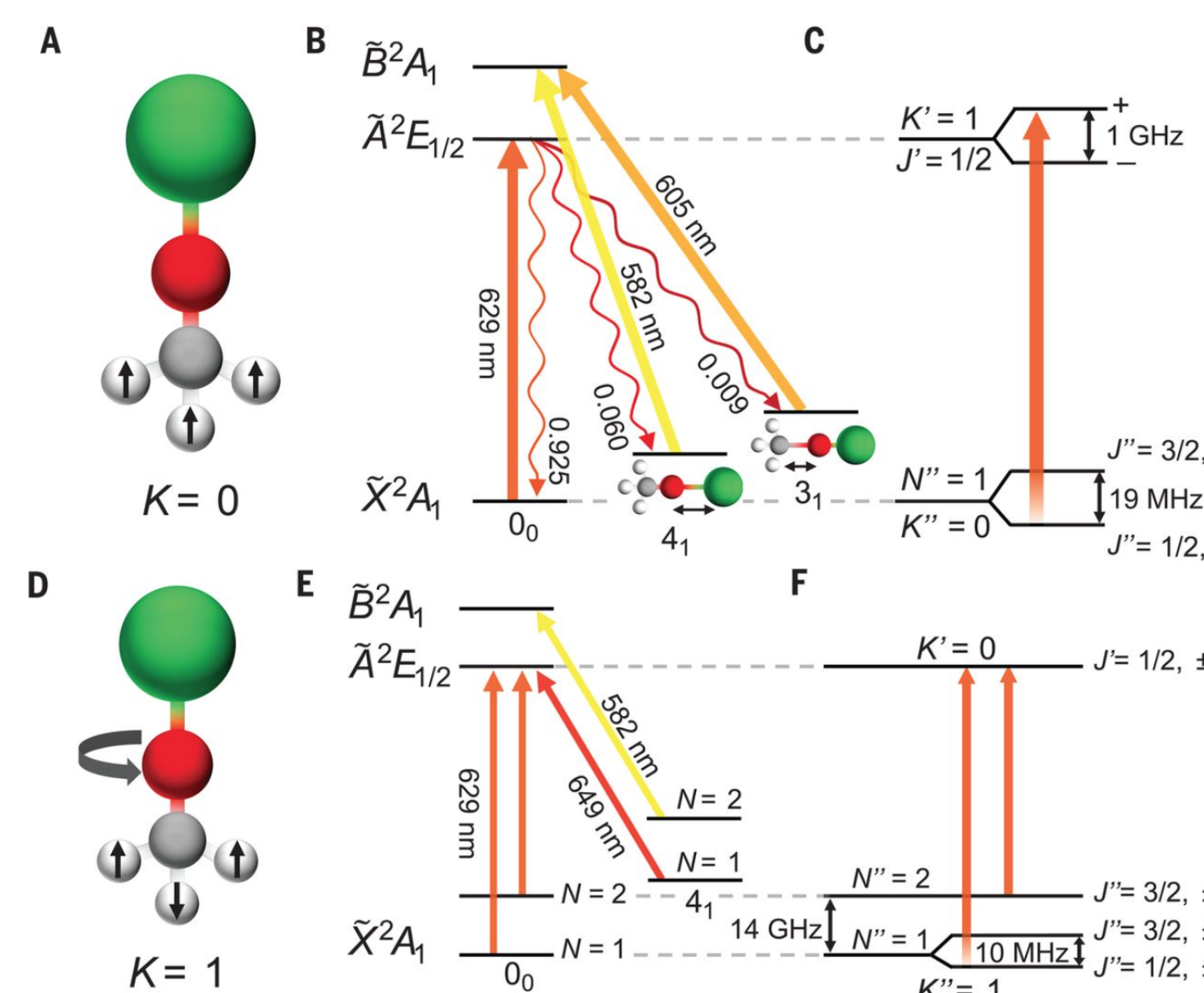


Fig. 5: CaOCH₃ molecule transitions

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.

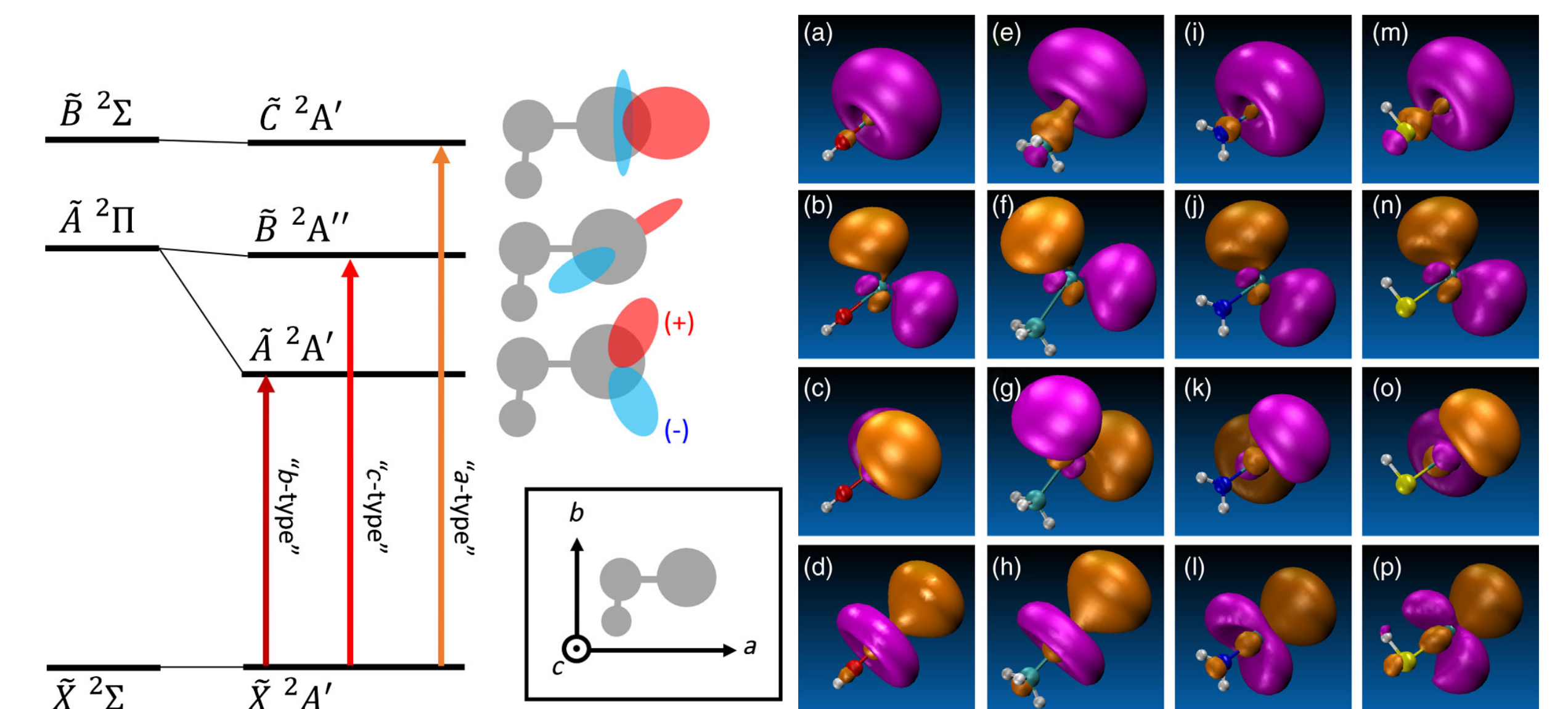


Fig. 6: **a** Representative energy-level diagram. **b**CaOH (a – d) CaCH₃ (e – h) CaNH₂ (i – l), and CaSH(m – p) [5]

- Breaking of cylindrical symmetry lifts orbital degeneracy and $\tilde{A}^2\Pi$ splits in 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]. Further work can be done to compare the theoretical approximation with experimental data.
- 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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- [3] Augenbraun, B. L., Frenett, A., Sawaoka, H., Hallas, C., Vilas, N. B., Nasir, A., ... Doyle, J. M. (2021). Zeeman-Sisyphus deceleration of molecular beams. Physical Review Letters, 127(26), 263002.
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