

Enlarging the Periodic Table of Laser-Cooled Molecules

A class of molecules with two valence electrons has been laser cooled and trapped for the first time.

By **Debayan Mitra**

Over the past 70 years, physicists have developed laser-based methods for controlling atoms and molecules, but much of this success has been concentrated on a few columns of the periodic table. For molecules, laser cooling has been limited to diatomic species

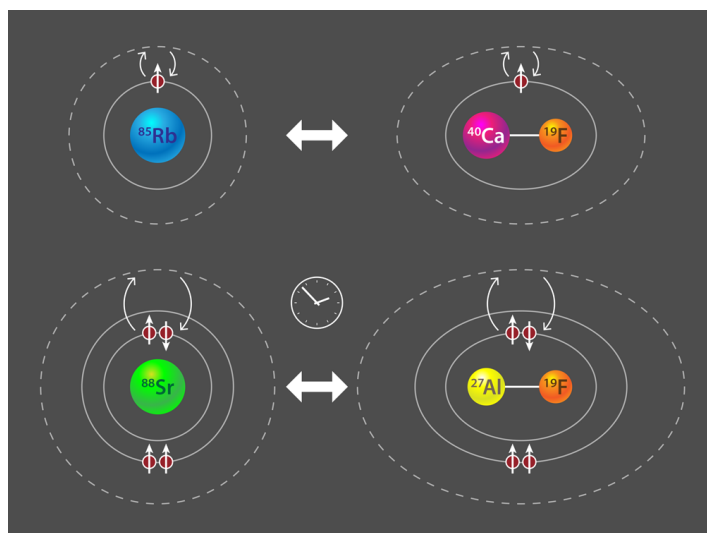


Figure 1: Laser cooling of atoms progressed from elements with one valence electron (top left) to two valence electrons (bottom left). Now with molecules, researchers are going from molecules with one valence electron (top right) to molecules with two valence electrons (bottom right). In each case, the cooling relies on a transition from the ground state to an excited state (shown as a dashed-line orbit). However, the two-valence systems also have a long-lived triplet state (shown with two spin-aligned electrons), whose transitions can be used in precision clock experiments. Credit: APS/**Alan Stonebraker**

that have a single unpaired valence electron for interacting with light. Extending laser cooling to molecules with two valence electrons has long been sought after (Fig. 1). The most promising nonreactive candidates are diatomic molecules that partner a halogen, such as fluorine (F) or chlorine (Cl), with a *p*-block atom, such as aluminum (Al) or thallium (Tl). Several research groups have specifically targeted AlF, AlCl, and TlF, but these molecules are difficult to work with because of their deep-ultraviolet transitions, complicated energy-level structures, and small magnetic moments. After years of effort, Eduardo Padilla-Castillo from the Fritz Haber Institute in Germany and colleagues have now laser cooled and trapped the molecule AlF [1]. This breakthrough paves the way for dense, cold samples that would be ideal starting points for evaporative cooling to a Bose-Einstein condensate.

The effort to control nature at the atomic level began in the second half of the 20th century with the advent of laser cooling. By shining a resonant beam of photons at a beam of atoms, one can counterintuitively cause the atoms to come to a standstill. This technique was remarkably efficient at cooling alkali-metal atoms (lithium, potassium, rubidium, and the rest of the first column of the periodic table) to near absolute zero. Physicists were suddenly able to achieve extremely low temperatures that cannot naturally exist anywhere else in the entire Universe!

Slowly but surely, this powerful tool matured in the early 21st century, extending its use across the periodic table to alkaline-earth atoms (like calcium and strontium), lanthanides (like ytterbium and erbium), transition metals (like titanium and silver), and noble gases (like helium and neon). Each additional class of atoms brought unique features that led to new

applications, such as optical atomic clocks and quantum simulators.

In 2004, Michael Di Rosa from Los Alamos National Laboratory in New Mexico had an interesting thought: Let's bring molecules into the laser-cooling family [2]. The first step would be to find molecules whose electronic structure allows lasers to excite their valence electrons. But molecules have rotational and vibrational degrees of freedom that atoms lack. For a molecule to be compatible with laser cooling, it must have special properties that ensure that it decays back to its original rovibrational state after each excitation.

Faced with these limitations, researchers initially focused on molecules with a single unpaired valence electron, as the alkali metals have. The first success came with strontium fluoride [3], which was quickly followed by calcium fluoride [4, 5] and by yttrium oxide [6]. Among the three, calcium fluoride (CaF) proved the most versatile, earning it the nickname “the rubidium of molecules.” CaF molecules have been trapped at microkelvin temperatures in rearrangeable optical tweezers, allowing two-qubit entanglement to be demonstrated [7].

The natural next step would be to consider molecules with two valence electrons, as strontium and the other alkaline-earth atoms have. Padilla-Castillo and colleagues set their sights on AlF. To reach the molecule's excited states, the researchers worked with industry to develop new high-power ultraviolet lasers based on frequency conversion. They produced an intense beam of AlF molecules using a cryogenic source on the basis of a nitrogen fluoride reaction with aluminum. The team performed extensive spectroscopy over several years to understand the complex electronic structure of AlF, especially in the context of laser cooling. Thanks to these and other efforts, Padilla-Castillo and colleagues were able to corral roughly 60,000 AlF molecules in a magneto-optical trap (MOT) at a temperature of about 14 mK.

Perhaps the most striking property of AlF is the existence of a nominally forbidden electronic transition (denoted as $a^3\Pi \leftarrow X^1\Sigma^+$), which is hindered from happening because it requires the spin of an electron to flip. This restriction causes the molecule's triplet state to have a long lifetime and hence a very small transition linewidth. The tiny linewidth benefits frequency-dependent Doppler cooling, which means the

molecules can be cooled to a lower temperature inside the MOT. But more importantly, it allows for the existence of a so-called clock transition (similar to the $^3P_1 \leftarrow ^1S_0$ transition in strontium), which could be useful for both timekeeping and precision measurements. Consequently, AlF is a prime candidate for the nickname “the strontium of molecules.”

This milestone of trapping AlF is one of many breakthroughs that bring us closer to realizing what could be called the new periodic table of molecules. Just as the 19th and 20th centuries saw the discovery and grouping of atoms with similar properties, now is the era of doing the same with molecules. Given that so many possible combinations of atoms are available, there's no hard limit to how large this new table will become. And there's also no restriction to small diatomic molecules. Recently, the polyatomic molecules calcium monohydroxide [8] and strontium monohydroxide [9] were trapped in MOTs, and the molecule calcium monomethoxide was laser cooled in one dimension [10]. These advances demonstrate the enormous power of laser cooling and the endless possibilities it presents.

Debayan Mitra: Department of Physics, Indiana University
Bloomington, Bloomington, IN, US

REFERENCES

1. J. E. Padilla-Castillo *et al.*, “Magneto-optical trapping of aluminum monofluoride,” *Phys. Rev. Lett.* **135**, 243401 (2025).
2. M. D. Di Rosa, “Laser-cooling molecules,” *Eur. Phys. J. D* **31**, 395 (2004).
3. J. F. Barry *et al.*, “Magneto-optical trapping of a diatomic molecule,” *Nature* **512**, 286 (2014).
4. S. Truppe *et al.*, “Molecules cooled below the Doppler limit,” *Nat. Phys.* **13**, 1173 (2017).
5. L. Anderegg *et al.*, “Radio frequency magneto-optical trapping of CaF with high density,” *Phys. Rev. Lett.* **119**, 103201 (2017).
6. A. L. Collopy *et al.*, “3D magneto-optical trap of yttrium monoxide,” *Phys. Rev. Lett.* **121**, 213201 (2018).
7. C. M. Holland *et al.*, “On-demand entanglement of molecules in a reconfigurable optical tweezer array,” *Science* **382**, 1143 (2023).
8. N. B. Vilas *et al.*, “Magneto-optical trapping and sub-Doppler cooling of a polyatomic molecule,” *Nature* **606**, 70 (2022).
9. Z. D. Lasner *et al.*, “Magneto-optical trapping of a heavy

polyatomic molecule for precision measurement,” **Phys. Rev. Lett.** **134**, 083401 (2025).

10. D. Mitra *et al.*, “Direct laser cooling of a symmetric top molecule,” **Science** **369**, 1366 (2020).