Light gives molecules the chills

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Arresting molecules

The endeavor of producing cold gaseous molecules dates back to at least the time when Kantrowitz and Grey dispersed "the myth of the cloud" (as John Fenn later called it) and thereby cleared the way for the coming of supersonic molecular beams [1]. These rapidly replaced effusive molecular beams, thanks to their high intensity and the added benefit of furnishing molecules that were *internally* cold. Molecular beams produced by the supersonic expansion of gas into vacuum were instrumental to the development of new research areas, among them high resolution molecular beam spectroscopy and molecular reaction dynamics. However, the *translational* energy of the supersonic beam molecules remained high. Meanwhile, the atomic physics community developed techniques to translationally cool atoms and even bring them to a grinding halt. These techniques were based on scattering of laser light by the atoms [2].

One variant of laser cooling is the so called Doppler cooling. When an atom moves towards a resonant laser beam, each absorbed photon imparts a kick to the atom in a direction opposite to the atom's motion. The re-emitted photons, however, scatter in all directions. The net effect is a slowing of the atom. When the laser beam acts on an ensemble of atoms, the ensemble's velocity distribution is narrowed down and the peak velocity shifted to lower values, which amounts to translational cooling of the ensemble. One photon kick changes the atom's velocity by only about 1 cm/s, so a lot of kicks are needed to significantly reduce the atomic velocity. This is quite feasible for strong transitions where more than 10^6 photons can be scattered in one second. However, a key requirement is that the transition be closed, ensuring that the atom is always returned to its original state at the end of the photon absorption-emission cycle. Herein lies the difficulty of laser-cooling molecules: It is the cycling transition allowing for a repeated scattering of same-wavelength photons that is so hard to come by in molecules, mainly due to their rich vibrational structure. Whereas one or two repumping lasers are usually needed to completely close an absorption-emission cycle in an atomic system, many dozens of repumpers would be needed for a typical molecular system [3], rendering laser cooling of molecules impractical. The lack of cycling transitions in molecules made molecular physicists scramble for alternative techniques. Leading among them are buffer gas cooling, Stark deceleration as well as photo- and magneto-association of pairs of ultracold atoms. These along with additional techniques have been recently reviewed on the pages of this journal [4].

However, last October, Edward Shuman, John Barry, and David DeMille from Yale University challenged the status quo in molecular cooling when they undertook a proof-of-principle experiment to laser cool SrF (strontium monofluoride) molecules [5]. Although SrF is one of a class of about a dozen other suitable diatomics, Shuman *et al.* have been able to demonstrate that laser cooling of molecules can work after all.

Ultracold molecular gases, particularly those made up of polar molecules such as SrF, offer enthralling prospects for fundamental studies of many-body physics. When two dipoles are oriented along the same direction, their interaction is repulsive when the dipoles are placed side-by-side and attractive when they are placed on top of each other. As a result, Bose-Einstein condensation (BEC) in a trapped gas of bosonic molecules interacting via dipole-dipole forces is strongly influenced by the trapping geometry and so can be switched on and off by an external knob. Apart from being anisotropic, the

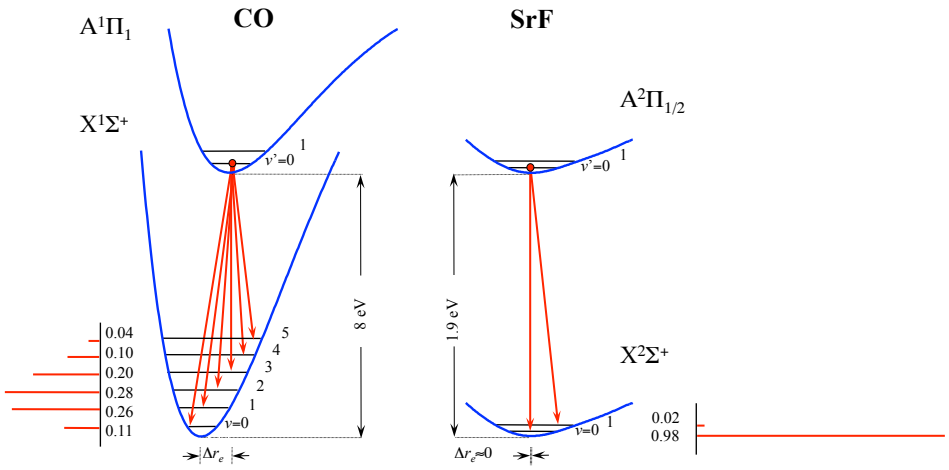

FIG. 1: Potential energy curves of the lowest electronic states along with the vibrational states they host for CO and SrF molecules. Red arrows show transitions between vibrational states, whose probabilities are given by the Franck-Condon factors (FCF) displayed by the red bars to the left and right. For SrF, the potential energy curves of the two electronic states shown have minima lying very nearly above each other, i.e., they have nearly equal equilibrium internuclear separations. According to the Franck-Condon principle, the most intense transition from the $v' = 0$ excited state then occurs to the vertically downward $v = 0$ state. The situation is quite different for CO, where the minima of the potential energy curves are displaced with respect to each other by 0.1 $\mathring{A}$, giving rise to a band progression in emission with $v' = 0$. Note that FCF's down to 10^{-5} are still of importance if the molecules are to be brought to a standstill.

dipolar interaction is also long-range. Cold dipolar gases of fermions are therefore prime candidates for attaining superfluid pairing in a single component gas. Furthermore, ultracold molecules have played an increasingly important role in testing fundamental symmetries (such as time-reversal symmetry, parity, or the Pauli principle), via precision molecular spectroscopy enhanced by the extended observation times available with cold molecules. Trapped polar molecules, entangled by the dipole-dipole interaction, are also considered for use as qubits in quantum computers. Details about experiments with, and theory and applications of cold molecules can be found in ref. [6].

Hope dies last

The opinion as to the feasibility of laser cooling molecules has turned in recent years, when several clever proposals were aimed at certain classes of molecules. First, Michael Di Rosa showed that monohydrides and monohalides have auspicious Franck-Condon factors (FCFs) that would allow molecules in vibrational levels of the excited electronic states to return almost exclusively to the ground vibrational level they were excited from [7]. Four years later, Jun Ye's group noticed that transitions to undesired rotational levels can be also largely precluded by choosing appropriate molecular states, namely those where the ground-state rotational quantum number is not lower than that of the excited-state [8].

The Yale group of David DeMille took these two important issues into consideration when selecting

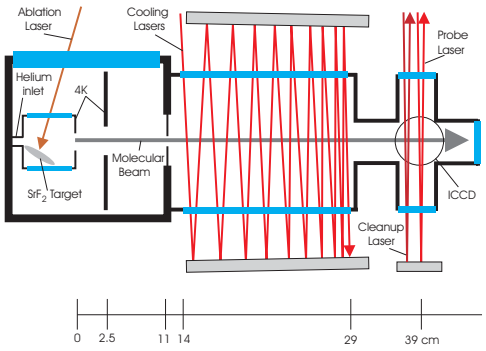

FIG. 2: In their experiment, the Yale group uses a cryogenic, buffer-gas cooled molecular beam of SrF. The buffer gas is a 4 K helium which thermalizes the SrF molecules produced by laser-ablating a solid SrF_2 precursor target. Several apertures placed downstream from the ablation area restrict the helium flow into the experiment and transversely collimate the beam. After exiting the cryogenic part of the apparatus, the molecular beam enters the cooling region where it is repeatedly intersected (about 75 times, in order to increase the interaction time) by the cooling lasers. Additionally, the cooling beams are nearly retro-reflected at the end of the cooling region, creating a standing-wave configuration. Just before probing the molecules, a "cleanup laser" pumps all the molecules into the lowest vibrational level. The last step is the detection of the molecules by imaging the $v = 0$ to $v' = 0$ laser-induced fluorescence onto a CCD camera, which provides information about their velocity distribution and thus temperature. Courtesy of Yale University. Reprinted with permission from the Nature Publishing Group, Supplementary Information to ref. [5].

SrF for their experiment. As shown on the right-hand side of Fig. 1, the FCF for the $v' = 0$ to $v = 0$ transition is 0.98, with the rest of the molecules decaying primarily to the $v = 1$ level. In contrast, for a benchmark diatomic molecule such as CO, fluorescence from the $v' = 0$ level populates the first six vibrational levels of the ground state (see left-hand side of Fig. 1). This is exacerbated by the inconvenient wavelength of 151 nm for the depicted CO transition, which is difficult to access with laser light. Here SrF offers another pleasant surprise, as all frequencies needed for cooling and vibrational repumping fall into the 660-685 nm range which is easily covered by diode lasers. The group first demonstrated optical cycling of about 150 photons by using the minimum of two diode lasers [9, 10], and then proceeded to adding a third laser, which significantly increases the number of scattered photons to 10^3 and thus enables Doppler cooling. Scattering of about 10^5 photons is expected to become feasible in the near future.

Having solved the vibrational and rotational issues by making some clever choices, the next obstacle is the hyperfine structure of the ground state caused by the nonzero nuclear spin of the molecule. In the case of SrF, the $N = 1$ ground level splits into four hyperfine components, while the $N = 0$ excited level has two hyperfine sublevels. The Yale researchers found an ingenious solution to simultaneously drive all four ground-state hyperfine levels, by passing the laser beams through an electro-optic modulator. This created frequency sidebands suitably spaced to match the hyperfine splitting.

The last key issue are the dark Zeeman sublevels that molecules could stray into while following the dipole selection rules, without the possibility of being returned to the closed absorption-emission cycle. The Zeeman degeneracy can be lifted by using either a pulsed electric field or a magnetic field. The latter approach was adopted for SrF, where a weak applied magnetic field of a few Gauss helped bring the molecules back into bright states. Not surprisingly, a theoretical account of what is going on becomes quite involved, as it has to include all 44 participating levels (3 ground states with 12 Zeeman levels each and 2 excited states with 4 Zeeman levels each) as well as all 12 driving laser frequencies (3 lasers with 4 sidebands each).

Interestingly, the needed magnetic remixing of Zeeman levels coupled with the standing-wave configuration used in the experiment, see Fig. 2, enables another cooling mechanism, the so called Sisyphus

cooling. As the ground state energy levels are perturbed by the laser light in a periodic manner (AC Stark shift), this leads to a periodic variation of their coupling to the excited state. A molecule moving up and down these potential energy hills and valleys will lose a net amount of its kinetic energy only if it absorbs a photon while at the top of a hill followed by a spontaneous decay to the bottom of a valley. For a correct detuning of the laser light from resonance, the molecule's kinetic energy can thus be transferred to the radiation field. The Yale researchers have observed both Doppler and Sisyphus cooling in one dimension, depending on the value of the applied magnetic field and they are working toward a comprehensive description of the cooling forces. The lowest temperature they achieved so far is 300 μK, which gives new hope for a direct laser cooling of molecules in three dimensions.

Acknowledgments

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