REPORT

COLD MOLECULES

# An optical tweezer array of ultracold molecules

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**Ultracold molecules have important applications that range from quantum simulation and computation to precision measurements probing physics beyond the Standard Model. Optical tweezer arrays of laser-cooled molecules, which allow control of individual particles, offer a platform for realizing this full potential. In this work, we report on creating an optical tweezer array of laser-cooled calcium monofluoride molecules. This platform has also allowed us to observe ground-state collisions of laser-cooled molecules both in the presence and absence of near-resonant light.**

Ultracold molecules hold tremendous promise as a new quantum resource, with widespread applications in quantum simulation (*1*–*5*) and computation (*6*–*8*), ultracold chemistry (*9*, *10*), and precision measurements that probe physics beyond the Standard Model (*11*, *12*). For example, their rich internal structures give rise to long-lived states with tunable long-range interactions, which can be harnessed to build coherent quantum systems, including molecular qubits (*1*–*5*) and strongly correlated synthetic materials (*6*–*8*). Controlling molecules at the quantum limit, however, remains an experimental challenge despite major recent progress in cooling and trapping (*13*–*22*). A powerful approach that may bypass existing experimental hurdles is optical tweezer arrays of laser-cooled molecules. In this proposed approach (*5*), one can fully control and detect individual molecules. Such individual particle control is a key frontier in quantum science and engineering because it opens up the assembly of complex quantum systems from the bottom up, as demonstrated recently with atoms in rearrangeable optical tweezer arrays (*23*, *24*) and assembly of a molecule from two atoms (*25*). For molecules, the bottom-up approach of using tweezer arrays combined with laser-cooling is especially important because it does not rely on favorable collisional properties necessary for evaporative cooling and can thus be extended to many other molecular species, including polyatomic ones (*26*). Optical tweezer arrays of laser-cooled molecules may thus help to realize the full potential of molecules in quantum science.

Here, we report successful creation and detection of an array of ultracold calcium monofluoride (CaF) molecules trapped in optical tweezers. In addition, the capability of distinguishing between single and multiple molecules in tweezers allowed us to observe ground-state molecular collisions of laser-cooled molecules both in the presence and absence of near-resonant light.

The starting point of our experiment was a magneto-optical trap (MOT) of $10^4$ molecules in the ground electronic, vibrational, and first rotational ($X$, $v = 0$, $N = 1$) manifolds (*16*). The MOT density of $10^5$ cm$^{-3}$ is too low for direct capture into micrometer-sized optical tweezers. To reach loading probabilities of order unity, one would require densities of ~$10^{11}$ cm$^{-3}$, which is more than four orders of magnitude higher than the highest achieved MOT density for laser-cooled molecules (*16*). To overcome the low starting densities, we loaded the optical tweezers using a two-step approach. First, molecules were transferred from the MOT into an optical dipole trap (ODT) formed by a focused 1064-nm laser beam (Gaussian beam waist, 45 μm) in the presence of Λ-enhanced gray molasses cooling (Λ-cooling) light on the $X \rightarrow A$ transition (Fig. 1B) (*21*). Because the laser cooling continues to work inside the trap, large density enhancements can be obtained (*20*). The molecules trapped inside the 1064-nm ODT were subsequently transferred into the smaller micrometer-sized optical tweezers (780 nm), also with the aid of Λ-cooling.

In detail, after the molecules were loaded into the MOT, the MOT beams and magnetic gradients were switched off, and 100 ms of Λ-cooling was applied to load molecules into a 200-μK deep ODT. This produced trapped samples of ~100 molecules, with densities as high as $3 \times 10^7$ cm$^{-3}$ at temperatures of 20 μK. The trapped molecules were then transferred into the optical tweezer traps, which are formed by tightly focused 780-nm laser beams. The optical tweezers were projected through a high-resolution imaging path, created by incorporating a microscope objective into the experiment (Fig. 1A). Multiple optical tweezers are created by using an acousto-optical deflector (AOD). We controlled the positions and the depths of the tweezers with the radio frequencies and powers driving the AOD. Typically, we used a tweezer trap depth of 300 μK. To transfer

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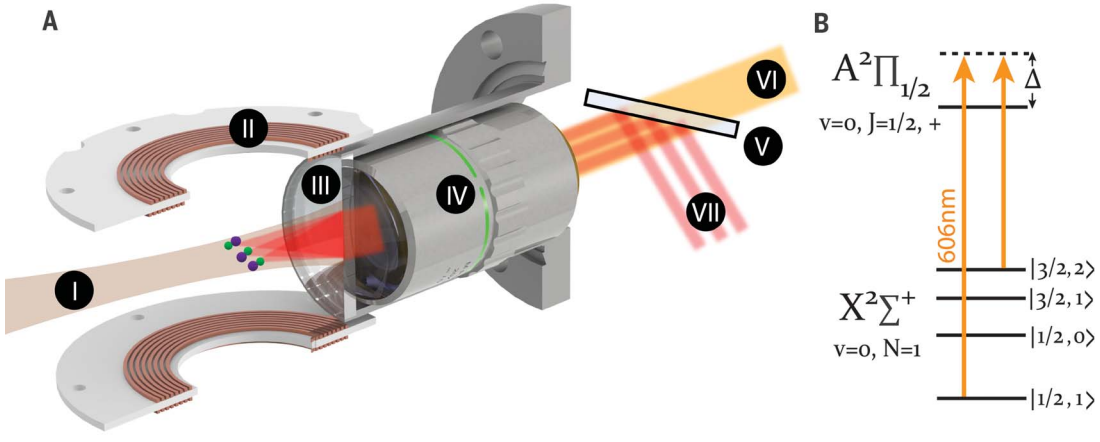


**Fig. 1. Molecular energy diagram and experimental setup.** (**A**) An optical dipole trap formed by a focused beam of 1064-nm light (I) intersects the MOT and is reflected off the re-entrant window (III) at an angle to prevent the formation of a lattice. A microscope objective (IV) is placed inside a re-entrant housing between the MOT coils (II). Fluorescence from the molecules (VI) is collected through the objective and imaged onto a camera. The optical tweezer traps are generated by using an AOD (VII) and are combined into the imaging path by using a dichroic mirror (V). (**B**) CaF level structure of relevant states used in the Λ-cooling process. The cooling is operated at a detuning $\Delta = 2\pi \times 25$ MHz.

molecules from the ODT to the optical tweezer, the Λ-cooling light was left on while the ODT power was ramped down over a few milliseconds. The ODT and the cooling light were then turned off in order for the remaining molecules to fall away.

The molecules in the optical tweezers were detected by means of Λ-imaging (*21*), in which Λ-cooling was applied, and the molecular fluorescence at 606 nm was collected through the microscope objective and detected on an electron-multiplying camera (EMCCD). We found that Λ-imaging remains effective for the tightly focused tweezer traps. Using an imaging duration of 30 ms, 2000 photons were scattered, of which 30 were detected. An average image of molecules trapped in an array of five optical tweezers is shown in Fig. 2A, as well a typical single-shot image with three occupied tweezers. We estimate a loading probability per trap of 34% (Fig. 2B), stemming from the stochastic nature of the loading process and limited initial densities. Because of light-assisted collisions, the probability saturates at 50%.

To characterize the tweezer traps and the molecular samples, we measured the radial trapping frequency $\omega_r$ by means of parametric heating and the molecular temperature with a release and recapture measurement (*27*). Using the trap frequency and the calculated ac polarizability of CaF at 780 nm, we determined that the tweezer traps have Gaussian beam waists of 2.3 μm, which is in agreement with the effective numerical aperture of the objective and measured optical aberrations arising from the re-entrant window. For the different hyperfine states, the polarizability varies up to 20%. The release and recapture measurements give a temperature of 80(20) μK, which is one-seventh of the tweezer trap depth and well below the Doppler limit (200 μK), verifying that Λ-cooling remains effective inside the tweezer traps. For two molecules, the peak trapped density is $3 \times 10^{10}$ cm$^{-3}$.

To ensure that at most one molecule was contained in each trap, we made use of light-assisted collisions in the presence of near-resonant light to "clean out" multiple occupancies, as is routinely done in atomic tweezer experiments (*28*). Inelastic loss from light-assisted collisions leads to a collisional blockade mechanism that ensures that the occupation of each tweezer trap is either one or zero (*29*). This provides a clean starting point, where uniform defect-free arrays of single molecules can be created simply by rearranging the positions of occupied traps.

In order to induce possible light-assisted collisions, we left the Λ-cooling light on for an additional 5 ms after loading. To determine whether multiple occupancies occur, we used background-subtracted single-shot images to produce histograms of photon counts in each tweezer trap. These histograms reveal a peak centered at zero counts corresponding to zero molecules, and a secondary feature with a peak centered around 1500 camera counts. To verify that this secondary feature corresponds to single molecules, we progressively reduced the loading rate into the tweezers by reducing the initial MOT number. As shown in Fig. 3, the center of the second feature remains unchanged, whereas its height decreases. When normalized to the area under the secondary feature, the second feature overlaps in all the histograms. This demonstrates that at most one molecule is present in each trap. If there were more than one molecule, the center of the secondary feature would move toward the zero-molecule feature as the average number in the tweezer is reduced.

These histograms also allow us to determine the detection fidelity for single molecules in a single shot. For each image, a tweezer trap was determined to be occupied if the number of photon counts exceeded a certain threshold. Owing to technical noise and background light, multiple photons per molecule were needed to make a determination, and higher fidelities were obtained with higher numbers of collected photons. Although the number of photons emitted can be increased with longer imaging durations, durations longer than the imaging lifetime of ~100 ms did not help because they led to increased background light. After optimizing the imaging parameters, we reached a detection fidelity of 92% at an optimal exposure of 30 ms.

To measure the rate of light-assisted collisions directly, we enlarged the size of the optical tweezer trap from 2.3 to 3.6 μm in order to lower the trapped densities and hence the collision rates. Lower collision rates provide a time window in which multiple molecules can be laser-cooled into the optical tweezer trap before collisional losses set in. We then studied the decay of multiple molecules by comparing histograms obtained after various Λ-cooling times. For short times, the histograms (Fig. 4, inset) display a long tail extending beyond the single-molecule peak, suggesting that multiple molecules were loaded. This long tail decays with longer Λ-cooling times, at a rate much quicker than that of the

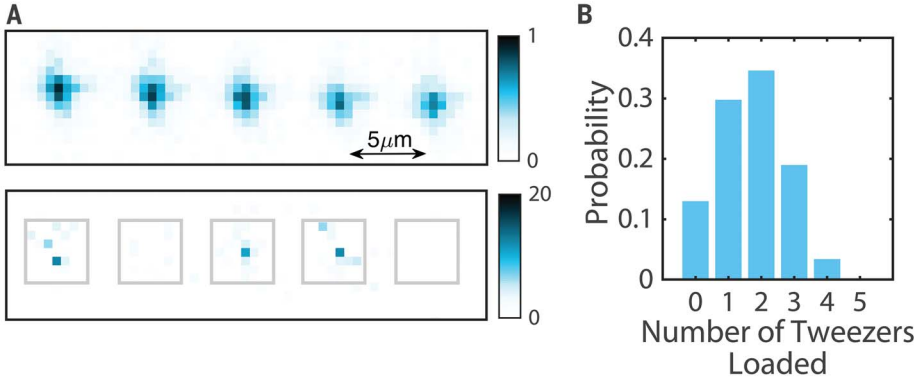


**Fig. 2. Molecule tweezer array.** (**A**) (Top) Image of optical tweezer array of single molecules, averaged over 500 shots. (Bottom) Single-shot image showing three occupied tweezer traps. The gray boxes represent the regions over which photon counts are summed. Color scale indicates signal per pixel. (**B**) Probability versus number of tweezer traps loaded. The average loading probability per trap is 34%.

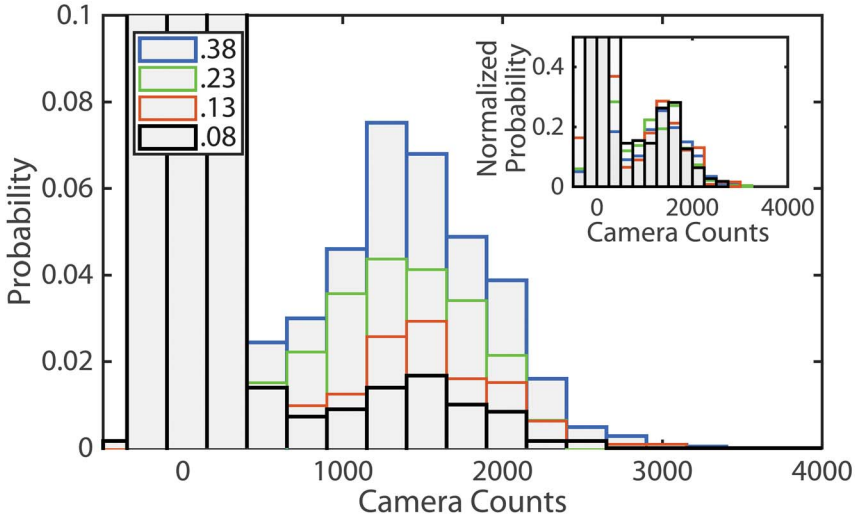


**Fig. 3. Histograms for single molecules.** Histograms with various tweezer loading fractions as indicated by the legend. (Inset) Histogram normalized by camera counts under the secondary feature.

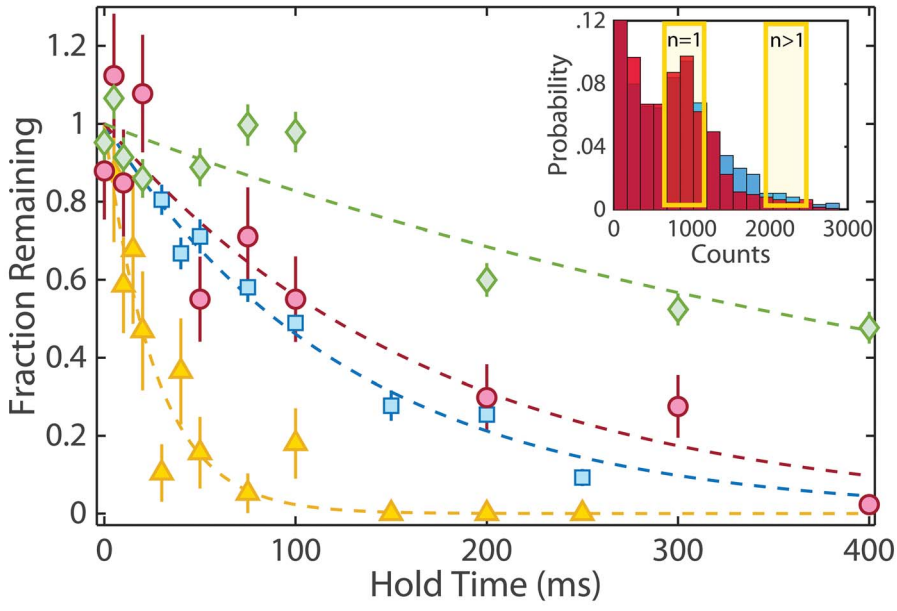


**Fig. 4. Molecular collisions in the tweezer loss curves for a single molecule and two molecules in the absence of light.** Green diamonds, single molecule; red circles, two molecules. The single-molecule lifetime is $\tau = 530$ ms, and the two-molecule lifetime is $\tau = 180$ ms. Loss curves for a single molecule (blue squares) and two molecules (yellow triangles) in the presence of Λ-cooling light reflect the imaging lifetime and light-induced collisional loss rate, respectively. The imaging lifetime is $\tau = 130$ ms, and the light-induced collision lifetime is $\tau = 26$ ms. (Inset) Histograms of camera counts after short (blue) and long (red) hold times. The highlighted region $n = 1$ denotes the range used to compute the fraction remaining for single molecules, and $n > 1$ denotes the range used to compute the fraction remaining for double molecules.

single-molecule peak. To quantify the loss rate, we cut the histogram to a region above the single-molecule feature (Fig. 4, inset) and measured the fraction within this range, $f_{n>1}$, which serves as a proxy for probability of loading more than one molecule. As shown in Fig. 4, the decay of $f_{n>1}$ as a function Λ-cooling time yields a $1/e$ lifetime of 26 ms. By comparison, the lifetime of single molecules in the presence of Λ-cooling time was 130 ms. This demonstrates that collisions were indeed occurring.

To determine whether collisions were occurring in the absence of light, we performed the same measurements by holding the molecules in the dark. In these conditions, the single-molecule lifetime was 530 ms (Fig. 4), whereas $f_{n>1}$ had a lifetime of 180 ms, which indicates that collisions were also present in the absence of light, albeit at a much lower rate. Because the collisional loss rate scales with molecular density, with the smaller 2.3 μm used in the array, Λ-cooling of a few milliseconds is sufficient to induce light-assisted collisions. This is consistent with the observed absence of multiple molecules in the smaller trap (Fig. 3). Assuming that the decay of $f_{n>1}$ is primarily from two molecules, we obtained a light-induced collision rate of $\gamma = 2.7(14) \times 10^{-8}$ cm$^3$ s$^{-1}$, corresponding to a cross section of $\sigma = 10(5) \times 10^{-10}$ cm$^2$. This is similar to that measured for rubidium (Rb) atoms in optical tweezers (*30*). Light-induced collisions arose from dipolar interactions, which resulted from an electric dipole moment induced by near-resonant light (*28*, *29*); this dipole moment has a similar size of about 1 debye in both atomic and molecular systems, suggesting that molecular systems should have similar collision rates to those of atomic systems. The light-assisted collisional cross section indicates a density limit of ~$10^{11}$ cm$^{-3}$ for the typical millisecond time scales for laser cooling. In the absence of light, the fitted loss rate is $\gamma = 4(2) \times 10^{-9}$ cm$^3$ s$^{-1}$, corresponding to a cross section of $\sigma = 1.4(7) \times 10^{-10}$ cm$^2$. There are multiple possible loss mechanisms, ranging from hyperfine and rotational relaxation to long-lived complex formation to simple elastic collisional loss; this requires further characterization. Controlled merging of singly occupied tweezer traps and internal state preparation (*5*) would provide a clean platform for such collisional studies (*25*).

By applying microwaves or dc electric fields, long-range dipolar interactions between single molecules could be engineered in future experiments. This paves the way for molecular tweezer arrays to be a quantum simulation and qubit platform with efficient state preparation and detection thanks to the inherent high signal from photon cycling, as in atoms. Future improvements could allow one to create much larger arrays, which is currently limited by available laser power. By improving the resolution of the imaging system used to project the tweezer traps, the trap power requirement can be reduced by at least an order of magnitude. Combined with higher laser powers, we estimate that one could create more than 100 traps in the near future. The methods we have developed in this work could also be extended to other laser-coolable molecules, including polyatomic ones, opening up a variety of applications, ranging from precision measurements (*12*, *26*, *31*) to ultracold chemistry (*9*, *12*, *32*).

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## SUPPLEMENTARY MATERIALS

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Supplementary Text
Fig. S1 to S6
Reference (*34*)

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**Tweezing cold molecules**

Arrays of optical tweezers have been used to trap atoms, but trapping and laser-cooling molecules in this setting is tricky. Such an approach would, however, be generalizable to many molecular species. Anderegg *et al.* created an optical tweezer array of calcium monofluoride molecules, which were laser cooled to their ground state (see the Perspective by Kotochigova). By distinguishing between single and multiple molecules in the tweezers, the researchers were able to observe molecular collisions. Boasting exquisite control over individual molecules, the optical tweezer array platform holds much promise for extending the applications of ultracold molecules.

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