A degenerate Fermi gas of polar molecules

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Experimental realization of a quantum degenerate gas of molecules would provide access to a wide range of phenomena in molecular and quantum sciences. However, the very complexity that makes ultracold molecules so enticing makes it hard to realize degeneracy an outstanding experimental challenge over the past decade. We now report the production of a degenerate Fermi gas of ultracold polar molecules of potassium-rubidium. Through coherent adiabatic association in a deeply degenerate mixture of a rubidium Bose-Einstein condensate and a potassium Fermi gas, we produce molecules at temperatures below 0.3 times the Fermi temperature. We explore the properties of this reactive gas and demonstrate how degeneracy suppresses chemical reactions, making a long-lived degenerate gas of polar molecules a reality.

Ultracold polar molecules are ideal candidates to realize a plethora of proposals in molecular and many-body physics. These include the development of chemistry in the quantum regime (I), the emulation of strongly interacting lattice spin models (2–6), the production of topological phases in optical lattices (7–10), the exploration of fundamental symmetries (11–15), and the study of quantum information science (16–18). Although magnetic atoms also exhibit long-ranged dipolar interactions and can be used to carry out these proposals (19, 20), polar molecules offer more tunable, stronger interactions and additional degrees of freedom. A low-entropy, quantum degenerate sample is a prerequisite for many of these explorations.

The intrinsic complexity of molecules relative to atoms, owing to the additional rotational and vibrational degrees of freedom, has made their cooling to ultralow temperatures one of the most substantial experimental challenges in molecular physics (21). Although the direct laser cooling of certain diatomic molecules has progressed enormously in recent times so that magneto-optical (22–25) and pure optical (26) trapping have been demonstrated, phase space density in these systems remains limited by the quantum degeneracy of the scattering process, which is still being investigated (29, 33, 38). Indeed, the lowest-entropy samples of ground-state molecules have been produced in a three-dimensional (3D) optical lattice, in which chemical reactions cannot occur, with an entropy of just 2.2 k_B (Boltzmann constant) per particle (39); however, producing quantum degenerate molecules in a bulk gas has so far been an outstanding experimental goal.

Here, we report the production of 10^5 fermionic ^40K^87Rb molecules at 250 nK and as many as 2.5 x 10^4 molecules at 50 nK, the latter corresponding to T/T_F = 0.3, where T_F is the Fermi temperature. Moreover, we observed that quantum degeneracy is accompanied by a suppression of chemical reactions. The efficiency of ultracold molecule production is limited at low temperatures by rapid three-body recombination of the atomic species as well as the spatial mismatch between atomic density distributions (40–42). For K^87Rb, however, in the limit where the K number vastly exceeds the Rb number, these effects can be mitigated, and the conversion to molecules with respect to the minority species can be high (42). Nonetheless, the gases are deeply degenerate, the atoms’ low entropy can be inherited by the molecules, resulting in a degenerate molecular gas (Fig. 1A).

After collecting ~10^9 ^87Rb atoms and 7 x 10^10 ^40K atoms in a vapor-cell magneto-optical trap, we cooled the atoms to degeneracy by performing radiofrequency evaporation in an optically plugged quadrupole trap followed by evaporation in a crossed optical dipole trap (xODT) (43). After optical evaporation was complete, the xODT was recompressed so that K experienced harmonic trapping frequencies of (ω_x, ω_y, ω_z) = 2π x (45, 250, 80) Hz, with gravity along the y direction. Trap frequencies are smaller by a factor of 0.72 and 0.79 for Rb and K^87Rb, respectively, owing to differences in mass and AC polarizability. Slices through atomic column-integrated density distributions after 16 ms time of flight (TOF) for three representative conditions are shown in Fig. 1B, top, and the corresponding numbers are given in Table 1. Among a number of technical improvements that allowed us to produce a deeply degenerate mixture with a large number of atoms, a key advance was the implementation of A–ejected gray molasses on the D2 (4^2S1/2 → 4^2P1/2) line of K (44) as well as the D3 (5^2S1/2 → 5^2P3/2) line of Rb (45).

We produced ground-state K^87Rb molecules by sweeping a magnetic field through an interspecies Fano-Feshbach resonance at B = 546.6 G to create weakly bound Feshbach molecules (Fig. 1A) (29). The molecules were then coherently transferred to the ground state by using STIRAP with ~90% efficiency. We conducted the experiments described here at zero electric field. The difference in trapping frequencies between molecules and atoms resulted in all three species having different equilibrium positions because of gravitational sag (46). Even though the molecules had the same initial temperature as the atoms, the initial nonequilibrium position set the molecules in motion, and the molecules in the gas rapidly heated up as potential energy was converted to kinetic energy. To mitigate this effect, before molecule production a 1D optical lattice of 30 molecular recoil energies was turned on against gravity. This ensured that the molecules and atoms were at equilibrium at the same position in the corrugated potential. After molecules were produced, unpaired atoms were quickly blasted away with resonant light (49), the lattice was then ramped off in 5 ms, and no spatial oscillations or rapid heating were observed. By varying the initial temperature and atomic number ratio, we generated molecular gases ranging from T/T_F greater than 1 to less than

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Three representative conditions are summarized in Table 1, and slices through molecular column density distributions after 10 ms TOF are shown in Fig. 1B, bottom; each molecular distribution shown was produced from the atomic conditions in Fig. 1B, top. Over this range, the average molecular density varies from $0.5 \times 10^{25}$ to $2 \times 10^{26} \text{ cm}^{-3}$.

At low $T/T_F$, the effects of degeneracy on the molecular velocity distribution after TOF are clear. Two-dimensional absorption images were collected and fit (47); the azimuthally averaged density profile of a cloud of KRb molecules after 10 ms TOF is shown in Fig. 2A. The profile is well fit by a Fermi–Dirac distribution [Fig. 2A, top, blue curve; $T/T_F = 0.31(2)$], whereas the classical Maxwell–Boltzmann distribution (Fig. 2A, top, red curve) overestimates the density at the center of the cloud and underestimates it in the wings. This is evident in the fit residuals (Fig. 2A, bottom), where the classical residuals exhibit ripples that are a hallmark of Fermi degeneracy (47). A Maxwell–Boltzmann fit to the wings of the profile (Fig. 2A, top, green curve), where the gas looks essentially classical, captures the temperature of the molecules but deviates at the center of the cloud.

The classical fit to the entire cloud systematically overestimates the temperature compared with the Fermi-Dirac fit because the Pauli exclusion principle prevents the multiple occupancy of low-energy states. The difference between the temperatures measured with the two fits is a strong indicator of the degree of quantum degeneracy (47). The normalized difference between them, $\delta U/U_\text{Cl} = 1 - T/T_{Cs}$, is shown in Fig. 2B for KRb as a function of $T/T_F$, where $T_{Cs}$ is the temperature determined from the Maxwell–Boltzmann fit. As $T/T_F$ is decreased, the normalized energy shows a deviation from the classical value, and for the most degenerate molecular clouds we currently produce, the deviation is larger than 30%. For comparison, the same quantity is shown for K at several values of $T/T_F$; both sets of data show good agreement with the theoretical prediction for an ideal Fermi gas (Fig. 2B, solid line).

Given the $T/T_F$ measured for K before molecular association, we expect an increase in the molecular $T/T_F$ by roughly a factor of 3 to 4 based on the change in particle number and trap frequency. However, we typically measured values of $T/T_F$ that were only a factor of 2.5 to 3 larger than that of K. At values of $T/T_F \leq 0.1$ for K, 85% of the Rb was condensed, and the Rb-to-K ratio was made to be roughly 1:10 (Table 1, third row) in order to minimize three-body recombination during magnetooassociation (42, 48). Under these conditions, molecules were produced with $T/T_F \leq 0.3$. Because the Rb BEC was fairly localized to the center of the K cloud (Fig. 1B), molecules were only produced in the lowest-entropy part of the Fermi sea (49), resulting in molecules that have a lower $T/T_F$ than expected from uniform K conversion over the entire distribution. At such low temperatures, the conversion from Rb to Feshbach molecules can be as high as 50%, indicating that there is good local phase space overlap between K and the Rb condensate. Because the density of the BEC is much higher than that of the K Fermi gas, the local conversion efficiency of K atoms approaches unity. This is the same principle of strong phase space matching that allowed for the efficient production of ground-state molecules in a 3D optical lattice (39). By contrast, at high $T/T_F$, where we produce the largest absolute number of molecules, conversion is typically 15% of Rb (Table 1, first row).

We produced degenerate molecules by adiabatically sweeping the magnetic field through a Fano-Feshbach resonance followed by coherent transfer to the ground state with high efficiency. Because the first step occurs on time scales that are comparable with the inverse trap frequency, the Feshbach molecules were produced at thermodynamic equilibrium (50). After transferring molecules to the ground state, we did not observe any large-scale spatial dynamics, suggesting that the ground-state molecular gas remains close to equilibrium. This was corroborated by the measured momentum distribution (Fig. 2A) and expansion energy (Fig. 2B). Furthermore, because inelastic collisions are predicted to be accompanied by a comparable number of elastic, momentum-exchanging collisions (51), this thermodynamic state is essentially maintained over the lifetime of the gas, as evidenced by the persistence of a low $T/T_F$, which grows slowly with

**Fig. 1. Production of degenerate molecules.** (A) Beginning with degenerate gases of Rb (red) and K (blue), Feshbach molecules are created by sweeping a magnetic field through a Fano-Feshbach resonance. The weakly bound molecules are coherently transferred to the ground state by using STIRAP. The resulting molecules reflect the degeneracy of their parent atoms. (B) Slices through images of atomic mixtures (two averages, 16 ms TOF, top) and ground-state molecules (four averages, 10 ms TOF, bottom) for molecular $T/T_F$ ranging from 0.3 to 1 (right to left). (Inset) False-color 2D column density, with blue corresponding to K and red to Rb. Dashed red lines correspond to noncondensed component of Rb cloud. The TOF images reflect the differing momentum distributions of the atoms and molecules.

<table>
<thead>
<tr>
<th>$T$ (nK)</th>
<th>Rb number</th>
<th>$T/T_c$</th>
<th>K number</th>
<th>$T/T_F$</th>
<th>KRb number</th>
<th>$T/T_F$</th>
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<tr>
<td>230</td>
<td>$6 \times 10^5$</td>
<td>$&gt; 1$</td>
<td>$1.2 \times 10^6$</td>
<td>0.3</td>
<td>$1.0(1) \times 10^5$</td>
<td>1.0(1)</td>
</tr>
<tr>
<td>110</td>
<td>$2 \times 10^5$</td>
<td>0.9</td>
<td>$1 \times 10^6$</td>
<td>0.2</td>
<td>$5(5) \times 10^4$</td>
<td>0.54(3)</td>
</tr>
<tr>
<td>50</td>
<td>$7 \times 10^4$</td>
<td>0.5</td>
<td>$5 \times 10^5$</td>
<td>0.1</td>
<td>$3(5) \times 10^4$</td>
<td>0.33(3)</td>
</tr>
</tbody>
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time (Fig. S2B) (43). This is further supported by the dependence of chemical reactions on degeneracy.

Given that KRb molecules are fermions, intermolecular scattering must occur in the p-wave channel because this is the lowest-energy antisymmetric collision channel. As such, the intermolecular potential (Fig. 3A) exhibits an antisymmetric collision channel. As such, the tunneling rate (and therefore reaction rate) is proportional to the temperature, so that chemical reactions must slow down at low temperatures (36). Examples of density loss curves and their corresponding fits for two temperatures are shown in Fig. 3B. At low temperature, the density decays at a slower rate compared with high temperature.

When a molecular collision leads to a reaction, the product molecules are ejected from the trap with high energy, leaving the remaining molecules unaffected because the mean free path is much larger than the size of the cloud. However, collisions tend to occur in the coldest, densest part of the cloud so that the lowest-energy molecules react and are lost preferentially, leading to anti-evaporation and an overall heating of the cloud. We typically observed heating linear in time, with rates ranging from $h = 10$ to $30$ nK/s, which is slightly larger than a simple anti-evaporation model would suggest (37). However, this rate is small enough for the molecular $T/T_F$ to remain close to its initial value over the molecules’ lifetime.

The reduction of density is determined by both the loss of KRb molecules and the increase in temperature. We fit our data to a simple twobody model that includes the effect of heating (36)

$$\frac{dn}{dt} = -\beta n^2 - 3 n \frac{dT}{2T}$$ (1)

where $n$ is the average classical molecular density of the bulk gas; the temperature is a measured, linear function of time, $T = T_0 + \Delta t$; and $\beta$ is the two-body loss coefficient. Because two-particle threshold behavior predicts $\beta = b T$, the fitting of the data with Eq. 1 allows us to determine $b$ (43).

Measurements of $\beta$ as a function of initial molecular temperature are shown in Fig. 4A. Data points with a blue face correspond to $T/T_F \leq 0.6$, and those with a red face correspond to $T/T_F > 0.6$; the solid red curve is the value predicted by multichannel quantum defect theory (MQDT), based on a previously published ab initio calculation of the van der Waals coefficient, $C_6$ (36, 54). The points with $T/T_F > 0.6$ follow the predicted MQDT trend closely, but those with $T/T_F \leq 0.6$ show deviations at all temperatures. Considering $b/T$, we observed a trend that is only dependent on $T/T_F$ and not initial temperature. We found that at $T/T_F \leq 0.6$, $b/T$ shows a strong deviation from the Bethe-Wigner threshold law, whereas above $T/T_F = 0.6$, $b/T$ is constant, with a measured value of $b/T = 0.84(6) \times 10^{-6}$ cm$^2$ s$^{-1}$ K$^{-1}$ (Fig. 4B, black line, error range shown in gray). This value is in excellent agreement with the predicted MQDT value (36, 54) of $b/T = 0.81(1) \times 10^{-6}$ cm$^2$ s$^{-1}$ K$^{-1}$ (Fig. 4B, red line). Our value is somewhat lower than the previously measured value of $b/T = 1.2(3) \times 10^{-5}$ cm$^2$ s$^{-1}$ K$^{-1}$ (36), with the discrepancy likely arising from the use of the corrugated potential to suppress gravitational sag in the current experiment.

Below $T/T_F = 0.6$, the measured $b/T$ drops to values as low as $0.21(8) \times 10^{-5}$ cm$^2$ s$^{-1}$ K$^{-1}$. A possible explanation for this observed deviation from a constant value is the change in density correlations as the gas becomes deeply degenerate. For a classical gas, the density sets the length scale of interparticle separation, which is much larger than the de Broglie wavelength, $\lambda$. In this case, large density fluctuations occur on the molecular scale, and two particles can easily find a configuration to scatter in the $p$-wave channel. In a degenerate Fermi gas, however, the probability of finding two molecules within a short distance of each other decreases as $T/T_F$ is lowered because of antibunching, with the average interparticle spacing being set by the de Broglie wavelength itself and ultimately by the Fermi wave vector, $2\pi/k_F$. This is the same physical phenomenon that gives rise to the Pauli pressure and reduced compressibility of a Fermi gas. This would cause an effective blockade that results in reduced density fluctuations (55–57) so that $p$-wave scattering and chemical reactions are suppressed beyond the Bethe-Wigner prediction. The suppressed collision rate manifests itself within our model as a reduction in the measured $b/T$ for the bulk gas, although the true two-body reaction rate constant is unaffected by degeneracy for any given molecular collision.
This effect is captured in the average relative number density fluctuation \(\langle \delta n^2(r) \rangle / \langle n(r) \rangle\), which is shown as a blue line in Fig. 4B as a function of \(T/T_F\). The curve is scaled to the MQDT value of \(\beta/T > 1\) but otherwise has no fitting parameters. That this simple consideration qualitatively describes the change in reaction rate suggests that the reduced particle fluctuations correspondingly reduce the probability of two molecules colliding, resulting in a suppression of chemical reactions. Density fluctuations are most strongly suppressed in the center of the trap (45), where the majority of chemical reactions occur, which is a possible explanation for why some points fall below the expected fluctuation suppression curve. Similar suppression of loss caused by strong correlations has been observed in the three-body recombination rate of a 1D Bose gas in which the particles have undergone fermionization (58). Furthermore, this effect is reminiscent of the reduction of the elastic s-wave collision rate observed in fermionic atoms (59, 60); however, in the elastic case, the reduction of the elastic cross section is attributed to the unavailability of empty states to scatter into, which is not relevant for inelastic collisions.

Although the qualitative agreement between the data and the suppression of density fluctuations is suggestive, a complete theory must treat the many-body nature of the degenerate gas within which the chemical reactions are taking place. In particular, it is important to consider the degree to which molecules thermalize after some are lost to chemical reactions. Furthermore, as \(T/T_F\) is decreased well below 0.3, collisions will be dominated by molecules near the Fermi surface so that the mean relative collision energy will deviate from the classical equipartition value to the quantum value of \(\hbar^2 k_B T_F\) per particle.

The production of a degenerate Fermi gas of polar molecules opens previously unexplored paths in ultracold molecular science. In a bulk gas, we now have the opportunity to study chemical reactions in a regime where quantum degeneracy and quantum fluctuations compete with classical chemical reaction dynamics. Furthermore, this work shows great promise for the exploration of degenerate molecules in electric fields, where the strong dipole-dipole interaction dominates. In this limit, we expect to see interaction-induced effects such as the deformation of the Fermi surface and the development of exotic many-body correlations.

**REFERENCES AND NOTES**


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Coaxing quantumness in a molecular gas

A dilute atomic gas cooled down to very cold temperatures can enter the so-called quantum degenerate regime, where quantum properties of the gas come to the fore. This regime has been achieved for both bosonic and fermionic atoms, but molecules, with their many internal states, present a special challenge. De Marco et al. cooled a bulk gas of fermionic potassium-rubidium molecules to quantum degeneracy (see the Perspective by Zelevinsky). The authors first cooled atomic potassium and rubidium gases separately, then bound them together into potassium-rubidium molecules, and finally brought the molecules down to their ground state. The density profile of the molecular gas revealed the system's quantum nature, which in turn kept the gas stable by suppressing chemical reactions.

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