Formation of Quantum-Degenerate Sodium Molecules

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Ultracold sodium molecules were produced from an atomic Bose-Einstein condensate by ramping an applied magnetic field across a Feshbach resonance. More than 10^5 molecules were generated with a conversion efficiency of $\sim 4\%$. Using laser light resonant with an atomic transition, the remaining atoms could be selectively removed, preventing fast collisional relaxation of the molecules. Time-of-flight analysis of the pure molecular sample yielded an instantaneous phase-space density greater than 20.

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Atomic Bose-Einstein condensates (BEC) provide a new window into macroscopic quantum phenomena [1]. A molecular condensate could lead to a host of new scientific explorations. These include quantum gases with anisotropic dipolar interactions, tests of fundamental symmetries such as the search for a permanent electric dipole moment, study of rotational and vibrational energy transfer processes, and coherent chemistry, where reactants and products are in coherent quantum superposition states. So far, the highly successful techniques for creating atomic BEC have not led to success for molecules. Laser cooling is difficult due to the complicated level structure of molecules [2], and evaporative cooling requires the preparation of a dense gas of molecules, where elastic collisions dominate inelastic collisions.

Alternative techniques, such as buffer gas loading [3] and Stark deceleration [4], have been successful in obtaining cold molecules. Yet these methods are still far from achieving the requisite phase-space density for BEC. The difficulty in cooling molecules directly can be circumvented by creating ultracold molecules from quantum-degenerate atomic samples. This requires molecule formation without release of energy, which can be accomplished either by photoassociation [5] or by "tuning" a molecular state via a Feshbach resonance [6] to be degenerate with the atomic state. A Feshbach resonance occurs when an applied magnetic field Zeeman shifts a molecular state to zero binding energy. By ramping an external field across a Feshbach resonance from negative to positive scattering length, translationally cold molecules in high vibrational states can be created adiabatically [7–9].

The first observation of a Feshbach resonance in ultracold atoms showed a high rate of atom loss [6,10]. Theories accounted for this loss by assuming the formation of ultracold molecules [7,8,11]. These molecules were predicted to decay vibrationally in less than 100 μs due to a two-body rate coefficient of order 10^{-10} cm^3/s. Because of this, no successful attempt was made to detect a molecular signature until atom-molecule beats were observed in ^{85}Rb, lasting about 100 μs [12]. Recent fermion experiments using magnetic field sweeps have observed molecules with lifetimes approaching 1 s [13–16]. Until now, similar experiments with bosons have been carried out only during ballistic expansion [17,18]. According to theory, the decay of molecules composed of fermionic atoms is suppressed by Pauli blocking [19], whereas molecules composed of bosons decay rapidly. This could explain the low conversion efficiency of about 5% for bosons, compared to $> 50\%$ for fermions, where more adiabatic field ramps are possible.

If highly degenerate atoms (both fermionic and bosonic) are converted adiabatically to molecules, the molecules can be created at a phase-space density exceeding 2.6, the critical value at which a uniform, ideal Bose gas condenses [20]. Previous experiments [14,18,21] have measured or estimated conditions close to or around this critical phase-space density.

Here we report the production of trapped sodium molecules from an atomic BEC. The initial phase-space density of the molecular sample was measured in excess of 20. High phase-space density could only be achieved by rapidly removing residual atoms, before atom-molecule collisions caused trap loss and heating. This was accomplished by a new technique for preparing pure molecular clouds, where light resonant with an atomic transition selectively "blasted" unpaired atoms from the trap. In contrast to spatial separation via a Stern-Gerlach method [17,18], this technique can separate out the molecules faster and does not require a large difference in the magnetic moments of the atoms and molecules.

To generate the molecules, sodium condensates in the $|F = 1, m_F = -1\rangle$ state were prepared in an optical dipole trap. The radial and axial trap frequencies of $\omega_r = 2\pi \times 290$ Hz and $\omega_z = 2\pi \times 2.2$ Hz, respectively, gave Thomas-Fermi radii of $R_r = 5$ μm and $R_z = 650$ μm, and a peak density of 1.7×10^{14} cm^{-3} for 5×10^6 atoms atoms. An adiabatic radio frequency sweep was used to transfer the atoms into the $|1, 1\rangle$ state, which has a 1 G wide Feshbach resonance at 907 G [6,22].

After 1 s equilibration in the optical trap, the molecules were generated using the field ramping scheme illustrated in Fig. 1(a). An applied magnetic field was ramped in ~ 100 ms to 4 G below the 907 G Feshbach resonance.

The field was generated using a pair of large bias and small antibias coils. Because molecules are only created when sweeping across the resonance from negative to positive scattering length, the field was stepped up to 913 G as quickly as possible (~ 1 μs) to jump over the resonance with minimal atom loss. After allowing 2.5 ms for transient field fluctuation to damp out, the field was ramped down in time τ_{down}. Because of atom-molecule coupling, part of the atomic population was transferred into the molecular state following the Landau-Zener avoided crossing. With the given width of the resonance and the atomic density, we use a simple Landau-Zener model to calculate a ramp speed of $\sim 10^4$ G/s to transfer roughly half the atoms to the molecular state [7,8,11]. However, inelastic collisions led to fast decay for both the atoms and the molecules near the resonance. We found that a faster ramp speed of $\sim 10^5$ G/s(corresponding to $\tau_{\text{down}} = 50$ μs) gave optimal results. The conversion efficiency of atoms to molecules was $\sim 4\%$. Slower ramp speeds resulted in a similar number of molecules, but at higher temperature [see Fig. 1(e)].

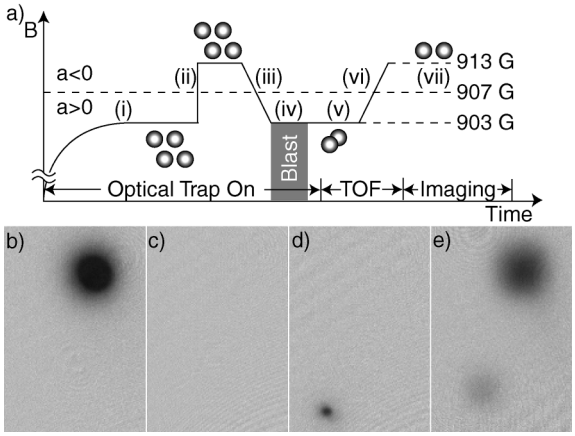

FIG. 1. (a) Experimental method for producing and detecting ultracold molecules. (i) Bose condensed atoms in an optical dipole trap are exposed to a magnetic field just below a Feshbach resonance. (ii) The field is quickly stepped through the resonance to minimize atom loss. (iii) The field is then swept back through the resonance, creating an atom-molecule mixture. (iv) Unpaired atoms are removed from the trap with resonant light, yielding a pure molecular sample. (v) The trap is switched off, allowing the molecules to expand ballistically. (vi) Finally, the magnetic field is swept back across the resonance to reconvert the molecules to atoms for imaging (vii). (b) Image of the *atomic* sample after ramping the field to produce molecules; (c) after the resonant light pulse has removed all unpaired atoms; (d) after the *molecules* ($\sim 10^5$) have been reconverted to atoms. (b),(c) were taken along the weak axis of the trap after 17 ms ballistic (time-of-flight–TOF) expansion. (e) An image showing both atomic (top) and molecular (bottom) clouds after 14 ms ballistic expansion, spatially separated by a magnetic field gradient. With 4 ms field ramp-down time, some molecules survived even without the blast pulse, but are much more heated. The field of view of each image is 1.8 mm $\times$ 1.3 mm.

The blast pulse was applied along the radial axis of the trap to minimize collisions between the escaping atoms and the molecules at rest. A 20 μs pulse of resonant light removed all atoms from the optical trap, leaving behind a pure molecular sample (see Fig. 1). At only 4 G below the Feshbach resonance, the light was still close to resonance with molecular photodissociation to low-velocity atoms, but the overlap matrix element was sufficiently diminished to leave the molecules unaffected. After a variable hold time, the optical trap was switched off and the molecules expanded ballistically for between 4 and 20 ms. The molecules were detected by converting them back to atoms with field ramp-up in $\tau_{\text{up}} = 100$ μs at the end of expansion. Varying τ_{up} between 50 μs and 4 ms did not affect the recovered atom number, though shorter τ_{up}'s recovered atoms with larger kinetic energy [23]. Thus we assume all molecules are converted back to atoms. A resonant absorption image was taken after an additional 500 μs, which allowed the imaging field to settle. The rapid conversion of molecules to atoms after a long expansion time ensured that the absorption images accurately depicted the momentum distribution of the *molecular* cloud.

Atoms and molecules were separated during the ballistic expansion by a Stern-Gerlach technique [Fig. 1(e)]. Because of trap imperfections, the large bias coils provided an additional radial gradient of the axial field of ~ 2.8 G/cm in the vicinity of the condensate. This value was determined from the trajectory of the falling atoms. Since the molecules have a different magnetic moment, they separate from the atoms during the ballistic expansion [Fig. 1(e)]. From the separation of the atomic and molecular clouds at different times, we determined the difference between atomic and molecular magnetic moments to be 3.2 μ_B (μ_B is the Bohr magneton), in good agreement with theory [11].

For different ramp down times τ_{down}, the time-of-flight images of the molecular cloud exhibit drastically different momentum distribution. The coldest cloud was obtained with the fastest ramp down time possible, $\tau_{\text{down}} = 50$ μs (Fig. 2). A Gaussian fit was used to determine the molecular temperature T_m and the phase-space density. Because of the rapid ramp down, the molecules had no time to adjust to the external trapping potential or any mean-field interactions. Therefore, we assume the molecules were *uniformly* created with the Thomas-Fermi profile of the original atomic BEC. The peak phase-space density is then given by

$$\text{PSD}_{\text{peak}} = \left(\frac{h}{\sqrt{2\pi k_B T_m M_m}}\right)^3 \frac{N_m}{\frac{8\pi}{15} R_r^2 R_z}, \qquad (1)$$

where h is the Planck constant, k_B is the Boltzmann constant, M_m is the molecular mass, and N_m is the number of molecules. The second factor in the equation is the peak density for a Thomas-Fermi profile.

Figure 3(a) shows the phase-space densities obtained for different holding time in the optical trap. Phase-space

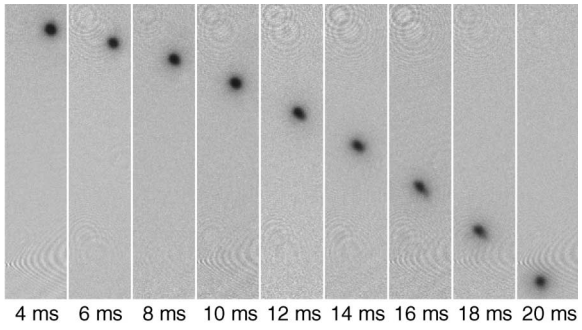

FIG. 2. Ballistic expansion of a pure molecular sample. Absorption images of molecular clouds (after reconversion to atoms) are shown for increasing expansion time after switching off the optical trap. The small expansion velocity corresponds to a temperature of ~30 nK, characteristic of high phase-space density. The images are taken along the weak axis of the trap. The field of view of each image is 3.0 mm × 0.7 mm.

densities in excess of 20 were observed, much larger than the critical value of 2.6. This demonstrates that a quantum-degenerate cloud of atoms can be transformed into a quantum-degenerate molecular gas.

The high initial phase-space density decayed rapidly (~2 ms), due to molecule loss and heating. For a pure molecular sample at a peak density of 4×10^{12} cm^{-3}, the molecule number dropped by half in 5 ms and the apparent temperature doubled in 2 ms. Since the molecules are formed in a high vibrational state with quantum number $v = 14$, losses are most likely due to vibrational relaxation. The high loss rate of the molecules is consistent with theoretically predicted two-body relaxation rate coefficients of 10^{-10} cm^3/s [9,24]. Because the loss of molecules is faster at the high densities near the bottom of the trap, it is accompanied by heating. This is in contrast to evaporative cooling, where the losses occur at the top of the trap. Such antievaporative heating gives a time constant 4 times slower than the observed heating rate. We therefore believe that the rapid increase in the apparent temperature is due to the inward motion of the molecular cloud (see below), and possibly transfer of the vibrational energy of the molecules.

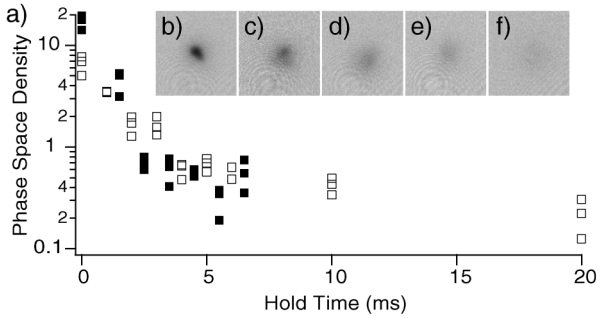

FIG. 3. Molecular phase-space density versus hold time. (a) The phase-space densities of the trapped molecules were observed to decrease significantly after a few milliseconds in the optical trap. The open and solid squares are data from two separate runs on different days. (b),(c) are absorption images of the molecular clouds after (b) 0 ms, (c) 2 ms, (d) 5 ms, (e) 10 ms, (f) 20 ms hold time in the trap. The field of view is 0.8 mm × 0.8 mm.

Our calculation of the phase-space density is conservative, since almost all errors lead to an underestimation of the value. The most critical quantity is the thermal velocity $v_{\mathrm{therm}} = \sqrt{2k_B T_m / M_m}$ obtained from the Gaussian fit of the cloud, since the phase-space density scales with the third power of v_{therm}. We determined the velocity by simply dividing the size of the cloud by the time-of-flight, without correcting for imaging resolution and initial cloud size.

Correcting for the imaging resolution of 10 μm compared to the typical cloud size of 50 μm would increase the phase-space density measurement by 6%. In addition, radial excitation of the trapped cloud (shown in Fig. 4) contributed to the size of the cloud after the ballistic expansion. From the fits, the smaller of the two Gaussian radii was used to calculate v_{therm}, assuming that the larger size was caused by radial excitations. Yet since the radial excitation can occur in two orthogonal directions, we estimate that the extracted thermal velocities were still overestimated by ~10%. We also considered magnetic focusing of the cloud due to residual field inhomogeneities. Because we use large coils (~17 cm in diameter and ~4 cm away from the condensate) to produce a homogeneous magnetic field, any residual radial curvature due to radial fields is calculated to be $\lesssim 0.1$ G/cm^2. An upper bound for the radial curvature of the axial fields was obtained from trap frequency measurements and ballistic expansion measurements as <1 G/cm^2. This can only reduce the size of the cloud by less than 2% after a typical ballistic expansion time of 17 ms.

We assume resonant absorption in determining the number of atoms. Any systematic effect such as small detuning or saturation, would lower both N_m and the Thomas-Fermi volume (proportional to $N^{3/5}$, where N is the number of condensed atoms). The net effect is an underestimate of the phase-space density. In addition, because the molecular formation process is nonlinear in

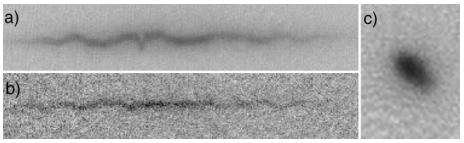

FIG. 4. Images of (a) atomic and (b) molecular clouds. These absorption images were taken after 7 ms ballistic expansion and show the axial extent of the clouds. Radial excitations in the optical trap resulting from the sudden switching of magnetic fields are manifest as snakelike patterns. Such excitations blur images (c) taken along the long axis of the trap (in 17 ms TOF), leading to an underestimate of the phase-space density. The fields of view are (a),(b) 0.6 mm × 3.2 mm, (c) 0.6 mm × 0.4 mm.

atomic density, the assumption of the atomic Thomas-Fermi volume for molecules is likely an overestimate. Furthermore, in the absence of strong mean-field repulsion (due to the much lower molecular density), the molecular cloud would not sustain the initial size of the atomic condensate [used in Eq. (1)], and shrink to a smaller size within a few milliseconds ($\sim$ radial trap period). If we assume radial thermal equilibrium while keeping the axial length fixed (as the axial trap period is 500 ms), the phase-space density would be 2 to 4 times higher than is shown in Fig. 3. To sum up, the extracted peak phase-space densities are underestimated by $\gtrsim 30\%$, and all other critical systematic effects would raise the value even further.

When a molecular cloud with high phase-space density equilibrates by elastic collisions, it should form a condensate. There is no prediction for the scattering length of the molecules, which are formed in the $|v = 14, l = 0\rangle$ state [25]. Assuming a prototypical scattering length of $100a_0$ (a_0 is the Bohr radius), we estimate the elastic collision rate between molecules to be 6 s^{-1}, which is smaller than our loss rate. Thus, the so-called ratio of good and bad collisions is smaller than 1.

Recent work on molecules composed of fermionic lithium [14,15] and potassium [26] atoms showed a dramatic increase in lifetime close to the Feshbach resonance. Theoretically, the rate of vibrational relaxation should decrease with the scattering length a_s as $\propto a_s^{-2.55}$ due to Pauli blocking [19]. In contrast, for molecules composed of bosonic atoms, the rate should increase proportionally to a_s [27]. On the other hand, the elastic collision rate is proportional to a_s^2, so for large a_s one would expect the ratio of good-to-bad collisions to exceed one. However, if this condition is met at loss rates faster than the trap frequency, the cloud can only establish local, not global equilibrium.

Whether our molecular sample is a condensate depends on one's definition of BEC. If phase-space density in excess of 2.6 (corresponding to a diagonal matrix element of the single-particle density matrix larger than 1) is sufficient, then one may regard a short-lived atom-molecule superposition state [12] as a molecular BEC. However, following this definition, a small excited state admixture in an optically trapped BEC would qualify as BEC of electronically excited atoms. If one asks for the additional requirement of a pure molecular sample, we have achieved that in this work. Another definition would require phase coherence, which could again be observed even in short-lived samples. Should one also require a lifetime of the degenerate sample exceeding the collision time (to achieve local equilibrium), the trap period (to achieve global equilibrium), or the inverse mean-field energy (the typical dynamic timescale)? In our opinion, BEC requires thermal equilibrium. High phase-space density is necessary, but not sufficient.

In conclusion, we have created a quantum-degenerate gas of 10^5 cold sodium molecules with a phase-space density >20. This was achieved with a fast magnetic field sweep through a Feshbach resonance, followed by quick removal of the remnant atoms with resonant light. This purification was necessary to avoid heating and decay of the molecules through inelastic collision processes. These processes could also be avoided by loading the atomic BEC into an optical lattice in the Mott-insulator phase with a filling factor of 2 [28,29] which, after sweeping the magnetic field through the Feshbach resonance, would result in a long-lived sample of isolated molecules.

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