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Bose-Einstein Condensation of Molecules

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We report on the Bose-Einstein condensation of more than 10^5 Li_2 molecules in an optical trap starting from a spin mixture of fermionic lithium atoms. During forced evaporative cooling, the molecules are formed by three-body recombination near a Feshbach resonance and finally condense in a long-lived thermal equilibrium state. We measured the characteristic frequency of a collective excitation mode and demonstrated the magnetic field–dependent mean field by controlled condensate spilling.

Since the first experiments on Bose-Einstein condensation (BEC) in ultracold atomic gases in 1995 (*1*–*3*), atoms of eight chemical elements have been condensed. BEC of more complex objects such as molecules or Cooper-paired atoms will open up many new avenues of research because they offer new degrees of freedom. An intriguing example is the fundamental change in quantum statistics when paired fermions form composite bosons. Recent experiments have demonstrated the formation of molecules in ultracold atomic gases of bosons (*4*–*9*) and fermions (*10*–*13*). Experiments starting with atomic BEC show the creation of molecular clouds at the threshold to quantum degeneracy (*7*) or clearly in that regime (*9*), but not in a thermal equilibrium state. In most of these experiments, weakly bound dimers are produced via magnetically tuned Feshbach resonances (*14*). Such a scattering resonance occurs when a free colliding atom pair energetically coincides with a bound molecular state. On the side of the resonance where the energy of the molecular level is below the dissociation limit, a weakly bound dimer state exists. The experiments indicate an important difference between weakly bound dimers composed of bosonic and of fermionic atoms. Dimers of bosons show a quick decay via inelastic atom-molecule or molecule-molecule collisions (*9*), so that quantum-degenerate molecular clouds can only be created in a transient regime. In contrast, the dimers of fermions exhibit a remarkable stability (*11*–*13*, *15*). Such molecular gases have been observed with lifetimes far longer than the time scales for elastic collisions and thermalization. This fact has been explained by a fermionic suppression of vibrational quenching in molecule collisions (*16*). Their stability allows us to use bosonic molecules composed of fermionic atoms to achieve molecular BEC in thermal equilibrium.

Our experiment is based on evaporative cooling of an optically trapped mixture of fermionic ^{6}Li atoms in the two lowest spin states (*11*–*13*, *17*–*21*). During the cooling process, a large number of bosonic dimers are formed by three-body recombination and finally condense into a molecular BEC. The spin mixture exhibits a broad Feshbach resonance at a magnetic field of about 850 G (*18*, *19*, *22*, *23*), which leads to a pronounced magnetic field dependence of the scattering length a (Fig. 1) that characterizes the s-wave interactions. Dimers in a single weakly bound state can be formed in the range of large positive a with a binding energy of $\hbar^2/(ma^2)$, where $\hbar$ is Planck's constant h divided by 2π and m is the mass of a ^{6}Li atom. This has been observed in magnetic field–dependent loss features (*24*) and changes in the interaction energy of the gas (*21*). Two recent experiments have directly demonstrated the presence of these molecules and investigated some of their properties (*12*, *13*). For negative scattering length, no weakly bound dimer state exists. For negative scattering length, where a weakly bound dimer state does not exist, the ^{6}Li gas exhibits a remarkable stability against collisional decay, and deeply degenerate Fermi gases have been created (*20*).

Our optical dipole trap is realized with a single Gaussian laser beam at a wavelength of 1030 nm, which is focused to a waist of 23 μm. At the full power of $P_0 = 10.5$ W, the radial and axial oscillation frequencies are $\Omega_r/2\pi = 14.5$ kHz and $\Omega_z/2\pi = 140$ Hz, respectively, and the atom trap is $U_0 \approx k_B \times 800$ μK deep (k_B denotes Boltzmann's constant). When the power P is reduced to a relative value $p = P/P_0$, the optical trap frequencies follow $p^{1/2}\Omega_i (i = r, z)$ and the trap depth for the atoms is $U_{at} = pU_0$. Our magnetic field B used for Feshbach tuning exhibits a curvature that gives rise to an additional contribution to the trapping potential. For the tight radial confinement of the optical trap, this effect is negligibly small. For the weak axis, however, a magnetic trapping effect becomes important with decreasing p. Taking this into account, the axial trap frequency is given by $\omega_z = \sqrt{p\Omega_z^2 + \omega_m^2}$. Here $\omega_m/2\pi = 24.5\ \text{Hz} \times \sqrt{B/\text{kG}}$ is the magnetic contribution, which is precisely known for our coils. For weak traps with $p \ll 0.03$ ($U_{at}/k_B \ll 25$ μK), the magnetic contribution dominates, and the axial confinement is harmonic with a corresponding frequency known on the percent level. In this regime, the mean trap frequency is given by $\bar{\omega} = (p\Omega_r^2\omega_m)^{1/3}$. For the weakly bound ^{6}Li dimers, all external forces are twice the ones on the individual atoms. Thus, the molecular trap is two times deeper than the atom trap ($U_{mol} = 2U_{at}$), and the trap frequencies are identical. Gravity is compensated for by a magnetic field gradient of 1.1 G/cm.

We start the evaporation process with $\sim 1.5 \times 10^6$ atoms at a temperature of ~80 μK, a peak number density of $\sim 10^{14}$ cm^{-3}, and a peak phase-space density of $\sim 5 \times 10^{-3}$. The mean elastic collision rate is as high as $\sim 5 \times 10^4$ s^{-1}. These excellent starting conditions are obtained by a two-stage loading process. The atoms are loaded into the dipole trap from another deep, large-volume standing wave trap (*25*), which itself is loaded from a magneto-optical trap. Forced evaporative cooling is then performed by reducing the trap power (*17*, *20*). We use a simple exponential ramp with a relative power $p(t) = \exp(-t/\tau)$, where the time constant $\tau = 0.23$ s is experimentally optimized. A feedback system allows us to precisely control the laser power to levels well below $p = 10^{-4}$.

BEC of weakly bound molecules occurs when we perform evaporative cooling at a large positive scattering length of $a \approx +3500a_0$, where a_0 is Bohr's radius. In this case, the evaporation process shows a strikingly different behavior in comparison with the corresponding situation at large negative scattering length, where no dimers can be produced.

First we discuss the creation of a degenerate Fermi gas without the possibility of molecule formation at a magnetic field of 1176 G, where $a \approx -3500a_0$ (*23*). Here the evaporation pro-

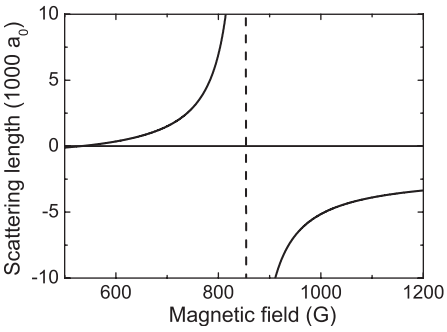

Fig. 1. Feshbach resonance at ~850 G in a mixture of the two lowest spin states of ^{6}Li (*18*). The s-wave scattering length a is plotted as a function of the magnetic field B.

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ceeds in a very similar way as that described in (*17*, *20*). The measured atom number N (*26*) first follows a scaling law $N/N_0 = p^{\alpha}$ (*27*), with $\alpha \approx 0.25$. In this regime, the temperature of the gas is typically a factor of 10 below the trap depth (*27*), and the elastic collision rate stays well above 10^4 s^{-1}. The crossover to Fermi degeneracy, where the thermal energy $k_B T$ reaches the Fermi energy $E_F = \hbar\,\bar{\omega}\,(3N)^{1/3}$, takes place at $p \approx 0.05$ ($U_{at}/k_B \approx 40$ μK). By further decreasing p, the trap depth $U_{at} \propto p$ decreases faster than the Fermi energy $E_F \propto p^{1/3}$. A threshold occurs when E_F reaches U_{at} and the trap is filled up to the "rim." Further decrease of p then leads to a spilling of atoms out of the trap and thus to a rapid decrease of N with p. Our data (Fig. 2) clearly show this spilling effect for $p < 1 \times 10^{-3}$ ($U_{at}/k_B < 800$ nK). Modeling the spilling curves provides us with an upper bound of $k_B T < 0.2 E_F$ for the temperature in terms of the Fermi energy. In the regime of a completely filled shallow trap, the number of atoms in the two-component spin mixture is given by two times the number of quantum states in the trap. A numerical calculation, shown in Fig. 2, confirms this interpretation of our data.

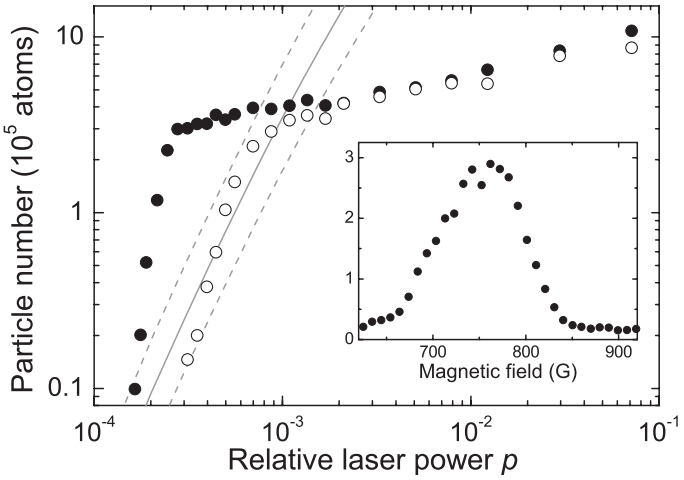

Fig. 2. Evaporative cooling results obtained on both sides of the Feshbach resonance. We measure the number of trapped particles (the number of all atoms that are free or bound in long-range dimers) as a function of the relative laser power p at the end of an exponential evaporation ramp $p(t) = \exp(-t/230\ \text{ms})$. The trap depth for atoms is $U_{at}/k_B = p \times 800$ μK, whereas for molecules it is two times larger ($U_{mol} = 2U_{at}$). The measurements taken at 1176 G with negative scattering length $a \approx -3500a_0$ (open circles) show the spilling of a degenerate Fermi gas when the trap depth reaches the Fermi energy. The solid line shows the maximum number of trapped atoms in a two-component Fermi gas according to a numerical calculation of the number of quantum states in our trap. The dashed lines indicate the corresponding uncertainty range due to the limited knowledge of the experimental parameters. The measurements at 764 G with positive scattering length $a \approx +3500a_0$ (solid circles) exhibit a striking increase of the trapped particle number at low values of p, which is due to the formation of molecules. The inset shows the optimum production of molecules in the magnetic field range where a weakly bound level exists. Here the total number of particles is measured for various magnetic fields at a fixed final ramp power $p = 2.8 \times 10^{-4}$ ($U_{mol}/k_B \approx 440$ nK).

The same evaporation procedure is performed at a magnetic field of 764 G, where the scattering length $a \approx +3500a_0$ (*23*) has essentially the same magnitude but opposite sign. Here the weakly bound dimers have a binding energy of ~2 μK, and their formation has been observed in several experiments (*12*, *13*, *21*). In order to detect the molecules, we dissociate them and measure the number of resulting atoms (*26*). For this purpose, we abruptly turn on the full trap power, which strongly heats the sample and leads to collisional dissociation. In order to ensure that we dissociate all molecules, we also apply a magnetic field ramp across the Feshbach resonance (*13*). The number of atoms measured after the dissociation process thus yields the number of free atoms together with atoms having formed molecules.

Below $p = 1 \times 10^{-3}$ the measured atom numbers (solid circles in Fig. 2) show a striking difference in comparison with the case of the degenerate Fermi gas. Down to a power level of $p = 3 \times 10^{-4}$ ($U_{mol}/k_B \approx 480$ nK), the trap holds almost all particles and contains up to 20 times more atoms than would be possible for fermions. Hence, the trapped sample can no longer be an atomic Fermi gas. The trap is filled with bosonic molecules in the weakly bound state (*28*). The lifetime of the molecular ensemble, for which we measure about 20 s at a fixed trap depth of $U_{mol}/k_B \approx 560$ nK, exceeds the time scale of elastic collisions (~100 μs) by several orders of magnitude. This highlights the fact that the molecular cloud exists in a thermal equilibrium state.

The formation of molecules during the evaporative cooling process can be understood in terms of a chemical atom-molecule equilibrium (*29*, *30*). Exothermal three-body recombination processes compete with dissociation by endothermal two-body processes. When the gas is cooled down, the equilibrium shifts to an increasing fraction of molecules. Because atom-atom, atom-molecule, and molecule-molecule collisions have comparable cross sections near the resonance (*16*), evaporation continues at about the same speed. In the final stage of cooling, all relevant energies, such as the thermal energy $k_B T$ and the trap depths U_{at} and U_{mol}, are far below the binding energy $\hbar^2/(ma^2)$, so that in chemical equilibrium one is left with an essentially pure sample of molecules. The fact that the binding energy of ~2 μK at our optimized magnetic field of 764 G is a few times larger than the final trap depth (inset, Fig. 1) fits well into this picture.

The observation that a large number of $N_{mol} \approx 1.5 \times 10^5$ molecules is confined in our very shallow, only 480 nK deep trap under thermal equilibrium conditions already shows that a molecular BEC is formed. The trap offers about 10 times more quantum states for dimers as compared to the case of atoms discussed before (*31*). Because we observe a factor of ~20 more particles than for the degenerate atomic Fermi gas, the molecular gas is necessarily quantum degenerate. Because of the high elastic collision rates, which stay well above 10^3 s^{-1} even for very shallow traps, the sample is also thermalized. The temperature then is a small fraction of the trap depth. According to standard evaporation theory (*27*), we can typically assume $T \approx 0.1\ U_{mol}/k_B \approx 50$ nK. This is well below the critical temperature for BEC, for which we calculate $T_C = \hbar\,\bar{\omega}\,k_B^{-1}\,(N_{mol}/1.202)^{1/3} = 280$ nK. Because the condensate fraction is given by $1 - (T/T_C)^3$, these arguments show that the molecular BEC must be almost pure.

To investigate the molecular condensate, we have studied a characteristic collective excitation mode (*32*, *33*). For a cigar-shaped sample in the Thomas-Fermi limit, well fulfilled in our experiment, such a quadrupolar mode is expected at a frequency of $\sqrt{5/2}\,\omega_z = 2\pi \times 33.8$ Hz. We perform our measurement at $p = 3.5 \times 10^{-4}$ ($U_{mol}/k_B \approx 560$ nK) with a trapped sample of ~10^5 molecules. We apply a sinusoidal modulation to the magnetic field with an amplitude of 3.5 G to modulate the molecular scattering length $a_m \propto a$ (*16*) with a relative amplitude of about 5%. After 2 s of continuous excitation, we measure the remaining number of particles in the trap. The resonance manifests itself in a sharp dip in the number of particles (Fig. 3). The observed resonance frequency of 33.6 Hz is in remarkable agreement with the expectation. We point out that a noncondensed gas deep in the hydrodynamic regime would show a similar frequency of 33.2 Hz (*34*), but thermalization in our shallow trap excludes this scenario (*35*). The measured collective excitation frequency rules out a gas in the collisionless regime, which would show its resonant loss at $2\omega_z = 2\pi \times 42.8$ Hz, and thus again confirms the thermalization of the sample. The observed narrow resonance width of ~1 Hz shows a very low damping rate and is consistent with an almost pure BEC (*33*, *36*).

An essential property of a BEC is its mean field potential $U_{MF} = 4\pi n a_m\,\hbar^2/(2m)$ resulting

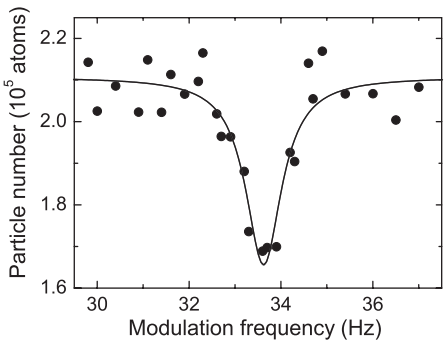

Fig. 3. Resonance of a collective excitation mode at $\sqrt{5/2}\,\omega_z$. The oscillation is excited by magnetic modulation of the molecular BEC mean field. The solid curve shows a Lorentzian fit to the data.

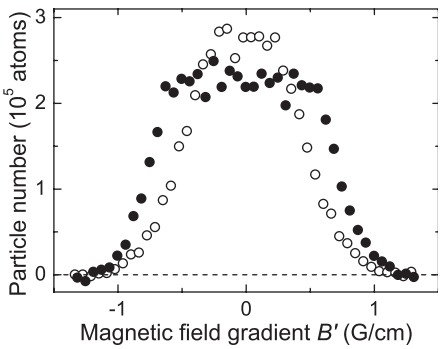

Fig. 4. Controlled spilling of the BEC by application of a magnetic field gradient B'. This variable gradient is applied in addition to the constant gradient of 1.1 G/cm that we use for gravity compensation. The data are taken at the two different magnetic fields $B_1 = 772$ G (open circles) and $B_2 = 731$ G (solid circles), where the mean field of the BEC is different by a factor of ~2.

from *s*-wave interactions; here n denotes the molecular density. For our molecular BEC with large positive a_m, the mean field is repulsive and thus stabilizes the BEC against collapse and decay. In a trap of finite depth, however, the mean field repulsion limits the maximum number of trappable molecules. When the chemical potential μ reaches the trap depth, a similar spilling effect is expected as we see for the Fermi gas, but for weaker traps. The decrease of our molecular signal (Fig. 2) below $p = 3 \times 10^{-4}$ ($U_{mol}/k_B \approx 480$ nK) may be explained by such a spilling effect.

We used spilling in a controlled way to demonstrate the mean field of the molecular BEC and to investigate its dependence on the magnetic field. After producing the BEC at a magnetic field of $B_1 = 772$ G and $p = 3.5 \times 10^{-4}$ ($U_{mol}/k_B \approx 560$ nK), we adiabatically tilt the vertical trapping potential by application of a magnetic field gradient B' that is smoothly ramped up within 50 ms. The number of remaining particles as a function of the applied field gradient (Fig. 4) shows the loss of molecules resulting from the reduced trap depth. When the magnetic field is kept at the evaporation field of $B_1 = 772$ G, where $a = 4100a_0$ (*23*), even very weak gradients lead to loss (open circles in Fig. 4). This indicates that the chemical potential is close to the potential depth, so that the trap is full. The chemical potential can be lowered by reducing the scattering length. For this purpose, we ramp the magnetic field to a smaller value. A spilling curve taken at $B_2 = 731$ G, where $a = 2200a_0$ (*23*), indeed shows a markedly different behavior (solid circles in Fig. 4). Here small gradients do not lead to any loss and the curve thus shows a flat top. For gradients $|B'|$ exceeding 0.65 G/cm, molecules get spilled until everything is lost at $|B'| = 1.3$ G/cm. The sharp onset of the spilling confirms the essentially pure nature of the BEC.

A comparison of the two spilling curves in Fig. 4 provides us with information on the ratio of the scattering lengths a_m at the two magnetic fields B_1 and B_2. In the spilling region above $|B'| = 0.65$ G/cm, the trap is full in both cases, and the trapped particle number is inversely proportional to a_m. Comparing the two spilling curves in that region, we obtain a scattering length ratio of $a_m(B_1)/a_m(B_2) = 2.4(2)$. This factor is indeed close to the factor of 1.9 (*23*) expected from the proportionality of atomic and molecular scattering lengths $a_m \propto a$ (*16*) and the dependence of a shown in Fig. 1. This observation demonstrates the mean field of the molecular BEC together with its magnetic tunability.

The ability to control interactions in a Bose condensed ensemble of paired fermionic atoms has many exciting prospects (*37*, *38*). It opens up unique ways to cool a fermionic gas far below the Fermi temperature (*39*) and to study different regimes of superfluidity (*40*–*43*). The experimental exploration of the strongly interacting crossover regime between a BEC-like and a Cooper-paired phase is a particular challenge and promises more insight into the physical mechanisms underlying superconductivity.

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