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Ultracold Triplet Molecules in the Rovibrational Ground State

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We report here on the production of an ultracold gas of tightly bound Rb_2 triplet molecules in the rovibrational ground state, close to quantum degeneracy. This is achieved by optically transferring weakly bound Rb_2 molecules to the absolute lowest level of the ground triplet potential with a transfer efficiency of about 90%. The transfer takes place in a 3D optical lattice which traps a sizeable fraction of the tightly bound molecules with a lifetime exceeding 200 ms.

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The successful production of quantum degenerate gases of *weakly bound* molecules has triggered a quest for quantum gases of *tightly bound* molecules. These can be used to investigate ultracold collisions and chemistry of molecules, to produce molecular Bose-Einstein condensates (BEC), and to develop molecular quantum optics. Standard laser cooling techniques as developed for atoms [1] do not work for molecules due to their complex internal structure. Other pathways to cold and dense samples of molecules are required, such as Stark or Zeeman deceleration [2,3] and sympathetic cooling [4] or association of ultracold atoms [5–7]. Association via Feshbach resonances [6,7] has directly produced quantum degenerate or near-degenerate ultracold molecular gases [8–12], but only in very weakly bound states with a high vibrational quantum number. Furthermore, such molecules are in general unstable when colliding with each other, particularly if they are composed of bosonic atoms.

Recently, optical schemes have been developed with the goal to selectively produce cold and dense samples of deeply bound molecules [13–18], ultimately in a rovibrational ground state. We report here the realization of this goal by optically transferring a dense ensemble of $^{87}Rb_2$ Feshbach molecules to a single quantum level in the rovibrational ground state of the Rb_2 triplet potential ($a\,^3\Sigma_u^+$). The transfer is carried out in a single step using stimulated Raman adiabatic passage (STIRAP) [14–16,19] with an efficiency of almost 90%, which is only technically limited. The molecules are held in a 3D optical lattice in which they exhibit a trap lifetime exceeding 200 ms, after an initial relaxation within 50 ms.

In contrast to singlet molecules, triplet molecules exhibit a magnetic moment giving rise to a rich energy level structure in the presence of magnetic fields. Thus, collisions of triplet molecules should exhibit magnetically tunable scattering resonances, e.g., Feshbach resonances. Molecules in the triplet rovibrational ground state can potentially relax to the singlet state $X\,^1\Sigma_g^+$ through inelastic collisions. This process has not yet been investigated and can possibly be suppressed. Such a regime would open

interesting prospects for future experiments with molecular Bose-Einstein condensates and ultracold chemistry [20].

The starting point for our transfer experiments is a 50 μm-size pure ensemble of 3×10^4 weakly bound Rb_2 Feshbach molecules, produced from an atomic ^{87}Rb Bose-Einstein condensate using a Feshbach resonance at a magnetic field of 1007.4 G (1 G = 10^{-4} T). They are trapped in the lowest Bloch band of a cubic 3D optical lattice with no more than a single molecule per lattice site [21] and an effective lattice filling factor of about 0.3. The lattice depth for the Feshbach molecules is 60 E_r, where $E_r = \pi^2\hbar^2/2ma^2$ is the recoil energy, with m the mass of the molecules and $a = 415.22$ nm the lattice period. Such deep lattices suppress tunneling between different sites. The magnetic field is set to 1005.8 G where the Feshbach molecules are in a quantum state $|f\rangle$ which correlates with $|F = 2, m_F = 2, f_1 = 2, f_2 = 2, \nu = 36, l = 0\rangle$ at 0 G [22]. Here, F and $f_{1,2}$ are the total angular momentum quantum numbers for the molecule and its atomic constituents, respectively, and m_F is the total magnetic quantum number; ν is the vibrational quantum number for the triplet potential and l is the quantum number for rotation.

For the transfer, we use a stimulated optical Raman transition. Two lasers (1 and 2) connect the Feshbach molecule level, $|f\rangle$, via an excited level, $|e\rangle$, to the absolute lowest level in the triplet potential, $|g\rangle$ [see Fig. 1(a)]. State $|g\rangle$ has a binding energy of 7.0383(2) THz × h and can be described by the quantum numbers $|F = 2, m_F = 2, S = 1, I = 3, \nu = 0, l = 0\rangle$ where S and I are the total electronic and nuclear spins of the molecule, respectively. At 1005.8 G, the ground state is separated by hundreds of MHz from any other bound level, so there is no ambiguity in what level is addressed. The level $|e\rangle$ is located in the vibrational $\nu' = 13$ manifold of the electronically excited $^3\Sigma_g^+$ $(5s + 5p)$ potential and has 1_g character. It has an excitation energy of 294.6264(2) THz × h with respect to $|f\rangle$, a width $\Gamma = 2\pi \times 8$ MHz, and a Zeeman shift of 3.4 MHz × h/G. From resonant excitation measurements, we deduce a coupling strength for the transition from $|f\rangle$ to
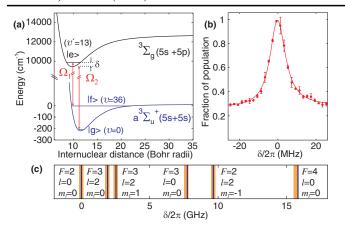
FIG. 1 (color online).   (a) Molecular levels of Rb$_2$. The lasers 1 and 2 couple the molecule levels $|f\rangle$, $|g\rangle$ to the excited level $|e\rangle$ with Rabi frequencies $\Omega_{1,2}$, respectively. Note the different energy scales for the ground and excited triplet potentials. (b) Dark resonance. The data show the remaining fraction of Feshbach molecules $|f\rangle$ after exposing them to both Raman lasers in a 3 μs square pulse. The two-photon detuning δ is scanned by varying the wavelength of laser 2 while keeping laser 1 on resonance. The Rabi frequencies are $\Omega_1 = 2\pi \times 0.7$ MHz and $\Omega_2 = 2\pi \times 10$ MHz. The solid line is a fit from a simple three-level model [14]. (c) Hyperfine and rotational spectrum for the $\nu = 0$ manifold of the $a\,^3\Sigma_u^+$ potential. The shaded bars correspond to measurements, and their width represents the typical error margin. The thin solid lines are from theoretical calculations and are shown with respective quantum numbers F, l, and its projection m_l. The line at $\delta = 0$ corresponds to state $|g\rangle$ and is the absolute lowest level of the $a\,^3\Sigma_u^+$ potential.

$|e\rangle$ of $\Omega_1/\sqrt{I_1} = 2\pi \times 0.4$ MHz$/\sqrt{\text{W cm}^{-2}}$ where Ω_1 is the Rabi frequency and I_1 is the intensity of laser 1. In comparison, the coupling strength for the transition from $|g\rangle$ to $|e\rangle$ is $\Omega_2/\sqrt{I_2} = 2\pi \times 30$ MHz$/\sqrt{\text{W cm}^{-2}}$. As in Autler-Townes splitting [11], we deduce Ω_2 from the measured width of a dark resonance which appears when both lasers resonantly couple to level $|e\rangle$ [see Fig. 1(b)].

The positions of the deeply bound energy levels of the Rb$_2$ triplet potentials $^3\Sigma_g^+$ and $a\,^3\Sigma_u^+$ were not precisely known before this work. Therefore, we have carried out extensive single- and two-color spectroscopy on our pure ensemble of Feshbach molecules. We have mapped out the vibrational progression of both potentials to the ground state ν $(\nu') = 0$ and find good agreement with theoretical calculations based on *ab initio* potentials [23]. In order to determine the hyperfine and rotational structure of the $a\,^3\Sigma_u^+$ vibrational ground state, we use a different intermediate level in the $^3\Sigma_g^+$ potential instead of $|e\rangle$. It has 0_g^- character and quantum number $I = 3$. Because of the selection rule $\Delta I = 0$ and the fact that I is a good quantum number for the deeply bound $a\,^3\Sigma_u^+$ states, this considerably restricts the number of observed lines. We find excellent agreement of the measured data with theoretical calculations based on a close-coupled channel model with

essentially no free parameters [see Fig. 1(c)]. In particular, we identify the lowest observed state $|g\rangle$ as absolute ground state of the $a\,^3\Sigma_u^+$ potential. A detailed discussion of further spectroscopic measurements as well as their analysis will be presented elsewhere.

STIRAP is a very efficient transfer method based on a stimulated Raman transition. It uses a counterintuitive pulse sequence during which molecules are kept in a dynamically changing dark superposition state $|\Psi_{ds}\rangle = (\Omega_2|f\rangle - \Omega_1|g\rangle)/\sqrt{\Omega_1^2 + \Omega_2^2}$. This dark state is decoupled from the light in the sense that there is no excitation of the short lived state $|e\rangle$, which suppresses losses during transfer [see, e.g., the dark resonance in Fig. 1(b)]. A vital condition for STIRAP is the relative phase stability between the two Raman lasers. Both of our Raman lasers, a Ti:Sapphire laser at 1017.53 nm (laser 1) and a grating-stabilized diode laser at 993.79 nm (laser 2) are Pound-Drever-Hall locked to a single cavity which itself is locked to an atomic ^{87}Rb-line. From the lock error signals, we estimate frequency stabilities on a ms time scale of 40 and 80 kHz for lasers 1 and 2, respectively. Thus, the transfer has to take place on a μs time scale in order not to lose phase coherence during STIRAP. Both laser beams have a waist of 130 μm at the location of the molecular sample, propagate collinearly, and are polarized parallel to the
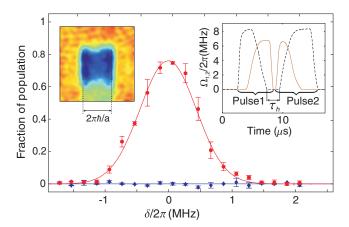

FIG. 2 (color online).   STIRAP. We plot the efficiency for population transfer from state $|f\rangle$ to state $|g\rangle$ and back with two STIRAP pulses (circles) as a function of two-photon detuning δ. In the dead time between the two STIRAP pulses, no Feshbach molecules can be detected (diamonds). The continuous lines are from model calculations as described in the text. The right inset shows the corresponding pulse sequence indicating the Rabi frequencies of laser 1 (solid line) and laser 2 (dashed line). The hold time τ_h, the time between the actual population transfers, is equal to 2 μs. The left inset is an absorption image which displays the atomic quasimomentum distribution in the optical lattice after the round-trip STIRAP transfer and subsequent adiabatic molecule dissociation. Atoms located in the inner square stem from the lowest Bloch band. $2\pi\hbar/a$ is the modulus of the reciprocal lattice vector.

direction of the magnetic bias field. Thus, the lasers can only induce π transitions.

We perform STIRAP by adiabatically ramping the Raman laser intensities as shown in the right inset of Fig. 2. Pulse 1 efficiently transfers the molecules from $|f\rangle$ to $|g\rangle$. In order to detect the molecules in state $|g\rangle$ after the transfer, we bring them back to $|f\rangle$ with a second, reversed STIRAP pulse sequence. We then dissociate the molecules into pairs of atoms at the Feshbach resonance. By releasing these atoms from the optical lattice in the manner described in [24], we can map out the Bloch bands in momentum space. After 13 ms of ballistic expansion, the corresponding atomic distribution is recorded with standard absorption imaging (see left inset in Fig. 2). For our signals, we only count atoms in the central square zone, corresponding to the lowest Bloch band [24].

Figure 2 shows the total transfer efficiency after two STIRAP transfers which are separated by a hold time $\tau_h = 2$ μs. The transfer efficiency for this *round-trip* STIRAP process is plotted as a function of the two-photon detuning δ and reaches about 75% at resonance ($\delta = 0$). Assuming equal efficiencies for both transfers, this corresponds to a single transfer efficiency of 87% and a total number of 2.6×10^4 molecules in state $|g\rangle$. We have experimentally verified that no molecules remain in state $|f\rangle$ between the two STIRAP pulses (diamonds in Fig. 2). Any such molecules would quickly be removed by laser 1 at the end of the first STIRAP pulse, which is kept on at maximum power for 1 μs after ramping down laser 2. Thus, all molecules that are retrieved after the second STIRAP transfer have been deeply bound in state $|g\rangle$. The 1 MHz width (FWHM) of the transfer efficiency is determined by power- and Fourier-broadening [25] and is in good agreement with a 3-level model (see solid lines in Fig. 2). We use a master equation which takes into account decoherence due to phase fluctuations of the Raman lasers [26]. These fluctuations can be expressed in terms of a short-term relative linewidth of the lasers, γ, which from fits, we determine to be about $2\pi \times 20$ kHz. Our calculations indicate that half of the losses are due to nonadiabaticity and half are due to the nonideal laser system. In principle, losses could also be due to other effects, such as coupling to levels outside of $|f\rangle$, $|e\rangle$, and $|g\rangle$. However, we have verified that this is not the case because losses due to optical excitation are completely negligible when we expose a pure ensemble of $|f\rangle$ ($|g\rangle$) molecules only to laser 2 (1). In addition, we did not detect any laser power dependent shift of the two-photon resonance within the accuracy of our measurements of $2\pi \times 200$ kHz.

We also investigate the dynamics and lifetime of the deeply bound molecules in the optical lattice. Because of their strong binding, molecules in state $|g\rangle$ cannot be expected to have a polarizability similar to that of Feshbach molecules, and it is not clear *a priori* what strength or even sign the optical lattice potential will

have for them. Indeed, as we show below, the lattice potential is attractive for the $|g\rangle$ molecules, but a factor 10 ± 2 shallower compared to the potential for the Feshbach molecules. Repeating the transfer experiment, we now vary the hold time τ_h between the two STIRAP transfers (see Fig. 3). Interestingly, for short hold times, the transfer efficiency exhibits a damped oscillation (see inset). The period and damping time are both about 80 μs. After 250 μs, the efficiency levels off at 40% and then decays much more slowly. The initial oscillation can be understood as follows. We consider the localized spatial wave packet of a Feshbach molecule at a particular lattice site in the lowest Bloch band. The first STIRAP transfer projects this wave packet onto the much shallower lattice potential felt by the $|g\rangle$ molecules. As a consequence, $|g\rangle$ molecules are coherently spread over various Bloch bands, and the wave packet undergoes ''breathing'' oscillations with the lattice site trap frequency ω_t. These coherent oscillations are damped by tunneling of $|g\rangle$ molecules in higher Bloch bands to neighboring lattice sites. The reverse STIRAP transfer maps this periodic oscillation back to the Feshbach molecules. Higher Bloch bands are populated here as well, but are at most partially counted in our
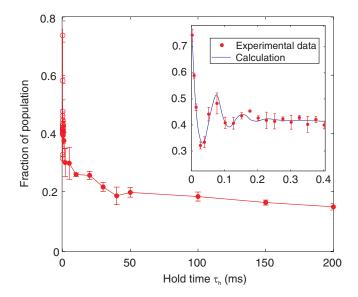

FIG. 3 (color online).　Dynamics and lifetime of $|g\rangle$ molecules in the optical lattice. We plot the transfer efficiency for the round-trip STIRAP process as a function of the hold time τ_h between the two STIRAP pulses. We only count molecules whose constituent atoms end up in the lowest Bloch band after transfer (see left inset of Fig. 2). Except for τ_h, all other experimental parameters are the same as in Fig. 2. Molecules are lost on three different time scales, 100 μs, 50 ms, and $\approx$200 ms. The inset zooms into the first 400 μs. The oscillations in the transfer efficiency are due to breathing oscillations of localized spatial wave packets of molecules in the lattice sites. The solid line is from a multiband model calculation. The data shown in the inset are plotted with open plot symbols in the main plot. The line connects neighboring data points.

scheme, which leads to an apparent loss of our transfer efficiency. We can describe the data well using a 3D multiband model (see solid line, inset Fig. 3). In this model, the states $|f\rangle$, $|e\rangle$, and $|g\rangle$ have a substructure due to the Bloch bands of the optical lattice, and the resulting levels are coupled by the laser fields. From fits to the data, we extract the trap frequency ω_t in a single lattice site, which determines the lattice depth for the molecules in state $|g\rangle$. We note that the earlier analysis of Fig. 2 does not include optical lattice effects. However, because the hold time τ_h is so short (2 μs), molecule signal losses due to oscillation amount to only 4%. In fact, the multiband model leads to the same theoretical curve as shown when we use a short-term relative laser line width $\gamma = 2\pi \times 18$ kHz, close to the previous value.

For longer hold times of up to 200 ms, Fig. 3 shows the time dependent loss of the deeply bound molecules. Within the first 50 ms, the fraction of recovered molecules drops to 20%. We attribute this loss mainly to the fact that all molecules in excited bands will simply fall out of the lattice since they are essentially unbound. For the remaining molecules in the lowest band, we find a lifetime exceeding our maximum experimental observation time which is limited due to heating of the magnetic field coils.

To conclude, using a nearly 90% efficient STIRAP transfer, we have created a dense and ultracold ensemble of deeply bound Rb_2 molecules in the absolute lowest quantum state of the $a^3\Sigma_u^+$ potential. These deeply bound molecules were trapped in a 3D optical lattice, and we observed coherent motional dynamics of their spatial wave packets in the sites. This indicates that besides the internal degrees of freedom, the external degrees of freedom are also precisely defined after transfer. The transfer of molecules into a single Bloch band should be possible, either by matching the lattice depths of weakly and deeply bound molecules, or by spectroscopically resolving the Bloch bands [27]. The latter involves longer STIRAP pulses and more tightly phase-locked Raman lasers, with the added benefit of increasing the transfer efficiency further. Investigating the collisional behavior of the triplet molecules will be the next goal as it is of central importance for ultracold chemistry [20] and for achieving molecular BEC. An appealing way to reach BEC is by melting an optical-lattice-induced Mott insulator of rovibrational ground state molecules [28]. For this, we have to improve the lattice occupation of our initial ensemble of Feshbach molecules [12] and use a selective STIRAP transfer to the lowest Bloch band.

During the preparation of our Letter, we learned that rovibrational ground state molecules have been produced with KRb [29].

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