



## Controlling the Hyperfine State of Rovibronic Ground-State Polar Molecules

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We report the preparation of a rovibronic ground-state molecular quantum gas in a single hyperfine state and, in particular, the absolute lowest quantum state. This addresses the last internal degree of freedom remaining after the recent production of a near quantum degenerate gas of molecules in their rovibronic ground state, and provides a crucial step towards full control over molecular quantum gases. We demonstrate a scheme that is general for alkali polar molecules and allows the preparation of molecules in a single hyperfine state or in an arbitrary coherent superposition of hyperfine states. The scheme relies on electric-dipole, two-photon microwave transitions through rotationally excited states and makes use of electric nuclear quadrupole interactions to transfer molecular population between different hyperfine states.

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The field of ultracold molecular quantum gases has recently seen tremendous progress through the preparation of near quantum degenerate ultracold and relatively dense gases of alkali molecules in the rovibrational ground state of the electronic ground molecular potential [1,2]. These experiments have demonstrated a high degree of control over the electronic, vibrational, and rotational degrees of freedom of ultracold molecules via two-photon optical Raman transitions [3,4], and the resulting ultracold ground-state molecules open the possibilities for long-lived quantum molecular gases, dipolar quantum gases (in the case of heteronuclear molecules such as KRb [1]), and ultracold chemical reactions. However, these ultracold ground-state molecule results [1,2] are insufficient in that the molecules were not shown to be in the absolute lowest energy state nor even in a single internal quantum state. The reason for this is that the hyperfine structure within a single rotational and vibrational level [5,6] was ignored. Indeed, these hyperfine degrees of freedom have also been largely ignored in theoretical proposals involving quantum gases of polar molecules [7]. This is a critical deficiency because, at the ultralow temperatures recently achieved for ground-state polar molecules, the energy splitting between hyperfine states can be much larger than typical collision energies in the gas. Moreover, as is well known in the context of ultracold atom gases, there is a fundamental difference between a quantum gas of particles in a single internal quantum state and an ultracold gas mixture of particles in multiple quantum states.

As is true for ultracold atomic gases, coherent control of this last remaining internal degree of freedom is essential for future experiments. For example, for experimental efforts to achieve a quantum molecular gas, namely, a Bose-Einstein condensate or quantum degenerate Fermi gas of ground-state molecules, it is advantageous to have all the molecules in a single hyperfine state, and ideally in

the hyperfine state with the lowest energy. Moreover, in the ultracold regime, quantum statistics play a significant role in collision processes [8]. Coherent control over the nuclear spin of the molecules could also open the door to the study of more complicated quantum gases where, for example, one might explore  $SU(N)$  magnetism [9]. For molecules, an additional possibility is quantum-state controlled ultracold chemical reactions, whose study will require reliable preparation and detection of the internal quantum state of the molecules [10]. Finally, the precise control over the hyperfine states could play a key role in quantum information schemes where one seeks to initialize and manipulate polar molecules as quantum qubits with long coherence times [11].

Here, we show that we can create ultracold KRb molecules in a single hyperfine state and, in particular, in their lowest energy state (electronic, vibrational, rotational, and hyperfine). In addition, we demonstrate a general scheme for coherently controlling the hyperfine degrees of freedom within the rovibrational ground-state manifold of alkali polar molecules. Using electric-dipole allowed rotational transitions, which have been previously exploited in molecular beam experiments to address different hyperfine states, we demonstrate quantum-state manipulation with a long coherence time that is only possible in the ultracold regime.

The lowest energy electronic potential for heteronuclear alkali molecules, such as KRb molecules, is a spin singlet state ( $X^1\Sigma^+$ ) that has zero electronic angular momentum and spin. Therefore, the hyperfine structure arises solely from the nuclear magnetic moments of the constituent atoms. Figure 1(a) shows a sketch of the hyperfine structure of rovibrational ground-state  $^{40}\text{K}^{87}\text{Rb}$  molecules at the experimentally relevant magnetic field of  $B = 545.9$  G (see below). The  $^{40}\text{K}$  atom has a nuclear spin of  $I^K = 4$ , while  $^{87}\text{Rb}$  has  $I^{\text{Rb}} = 3/2$ ; together, this gives a total of

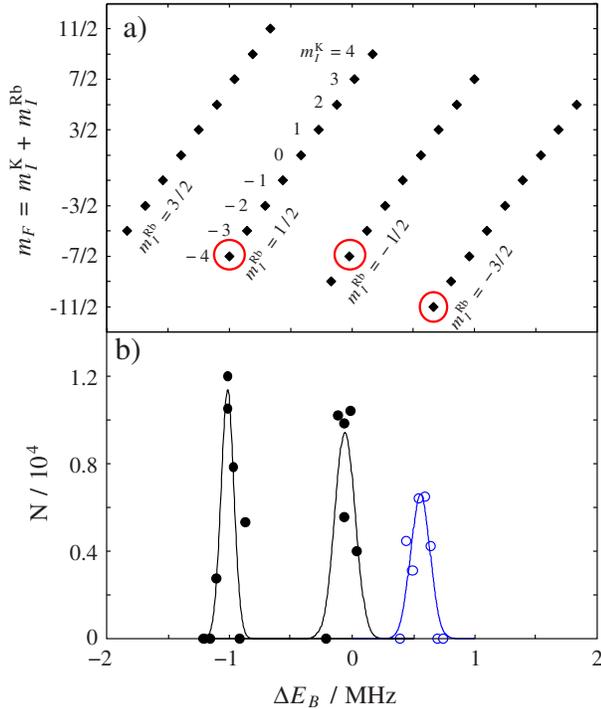


FIG. 1 (color online). (a) Hyperfine structure of  $^{40}\text{K}^{87}\text{Rb}$  molecules in their rotational ( $N = 0$ ) and vibrational ( $\nu = 0$ ) ground state of the electronic ground molecular potential ( $X^1\Sigma^+$ ) at  $B = 545.9$  G (see text). The circled quantum states can be directly populated via STIRAP in our experiment. (b) Optical two-photon spectroscopy of the rovibrational ground-state manifold of  $^{40}\text{K}^{87}\text{Rb}$  molecules (see text). We observe three hyperfine states, which are characterized by  $m_F = -7/2$  (black points) and  $m_F = -11/2$  (blue open points). Here,  $\Delta E_B$  is the binding energy of the hyperfine states at  $B = 546.9$  G relative to the binding energy of the rovibrational ground state at zero magnetic field. Negative  $\Delta E_B$  indicates a more deeply bound state and positive  $\Delta E_B$  a less deeply bound state.

$(2I^K + 1)(2I^{\text{Rb}} + 1) = 36$  hyperfine states for the rovibrational ground-state molecules. At sufficiently large magnetic fields (typically  $B > 20$  G), the nuclear Zeeman effect dominates over the coupling of the two nuclear spins to each other ( $c\vec{I}^{\text{Rb}} \cdot \vec{I}^{\text{K}} \ll g_I^{\text{Rb,K}}\mu_B\vec{I}^{\text{Rb,K}} \cdot \vec{B}$ , where  $c$  is the scalar nuclear spin-spin coupling constant). We therefore label the molecular hyperfine states with the quantum numbers  $m_I^K$  and  $m_I^{\text{Rb}}$  describing the nuclear spin projections onto the external magnetic-field axis.

We perform our experiments on a near quantum degenerate gas of polar  $^{40}\text{K}^{87}\text{Rb}$  molecules in the rotational ( $N = 0$ ) and vibrational ( $\nu = 0$ ) ground state of the electronic ground-state molecular potential ( $X^1\Sigma^+$ ) [1]. Starting from weakly bound  $^{40}\text{K}^{87}\text{Rb}$  Feshbach molecules formed in the vicinity of a Fano-Feshbach resonance at  $B = 546.7$  G [12,13], we subsequently transfer the molecules, at  $B = 545.9$  G, into the rovibrational ground state using a single step of coherent two-photon Raman transfer (STIRAP) [3]. The Raman process bridges an energy gap

of  $h \times 125$  THz and has a typical one-way efficiency of 80%.

The first question we consider is what hyperfine state or states are populated in the Raman process? We start with weakly bound Feshbach molecules prepared in a single quantum state with a total angular momentum projection of  $m_F = -7/2$  [13]. The two Raman laser beams are linearly polarized and copropagating parallel to the quantization axis defined by the external magnetic field. By conservation of angular momentum, the resulting  $X^1\Sigma^+$  ( $\nu = 0$ ,  $N = 0$ ) molecules are then restricted to  $m_F = m_I^K + m_I^{\text{Rb}} = -11/2, -7/2, -3/2$  ( $\Delta m_F = \pm 2, 0$ ). Just this consideration leaves eight possible hyperfine states for the ground-state molecules. However, the hyperfine structure in the electronically excited state used in the Raman process will in general impose additional selection rules. In the experiments, we have observed three accessible hyperfine states. As seen in Fig. 1(b), we can spectroscopically resolve the hyperfine states for a given  $m_F$  value. Based on two-photon selection rules and the binding energies of the hyperfine states, we can identify the states and assign the quantum numbers  $m_F = -7/2$  and  $m_F = -11/2$ . In particular, the fact that the highest energy state in Fig. 1(b) disappears for spectra taken with identical circular polarization for both Raman laser beams allows us to identify this state as  $m_F = -11/2$ .

Thus, we conclude that our two-photon Raman process, starting from a well-defined Feshbach molecule state, selectively populates a single hyperfine state within the rovibrational ground-state manifold ( $X^1\Sigma^+$ ,  $\nu = 0$ ,  $N = 0$ ). However, this state is not the lowest energy hyperfine state of the molecule. In the remainder of the Letter, we address

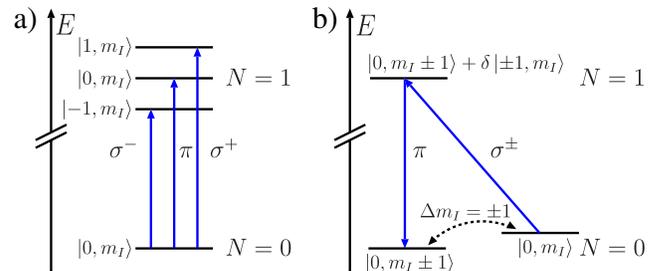


FIG. 2 (color online). (a) Electric-dipole transitions between the rotational ground state  $N = 0$  and the first rotationally excited state  $N = 1$ . To first order, electric-dipole transitions will keep the hyperfine state unchanged  $\Delta m_I = 0$ . (b) Controlling the hyperfine state within the rotational and vibrational ground state. The interaction between the nuclear electric-quadrupole moment of  $^{40}\text{K}/^{87}\text{Rb}$  and the electric-field gradient of the electronic cloud mixes quantum states with different nuclear spin quantum number  $m_I^{\text{K/Rb}}$  in  $N = 1$ . This allows the implementation of a two-photon scheme to transfer molecules between different hyperfine states within the rovibrational ground state ( $\Delta m_I^{\text{K/Rb}} = \pm 1$ ). To simplify the notation, we abbreviate  $|N, m_N, m_I^K, m_I^{\text{Rb}}\rangle$  by  $N |m_N, m_I\rangle$ . Here  $m_I$  refers to the changing hyperfine quantum number  $m_I$  of K or Rb.

the question of how to coherently manipulate the hyperfine state of our ground-state polar molecules and, ideally, how to coherently address any one of the 36 possible hyperfine states. As a starting point for further manipulation of the hyperfine state, we first prepare molecules in the lowest energy state in Fig. 1(b), which is characterized by  $m_I^K = -4$  and  $m_I^{\text{Rb}} = 1/2$ . *A priori*, manipulation of nuclear spin states of the molecule is difficult because of the weak coupling of the nuclear spin to external magnetic fields. In addition, transitions between quantum states with  $\Delta m_I = \pm 1$  are nearly degenerate, which presents an obstacle to driving selectively a single nuclear transition.

We manipulate the hyperfine state of the ground-state molecules using microwave transitions that couple the rotational ground state to a rotationally excited state. Figure 2 illustrates the basic idea for a two-photon microwave transfer scheme within the hyperfine structure of the rovibrational ground state. The permanent electric-dipole moment of polar molecules allows strong transitions between the rotational ground state and the first rotationally excited state. The single-photon electric-dipole transition has a Rabi frequency given by  $\frac{\vec{d} \cdot \vec{\mathcal{E}}}{\hbar}$ , where  $\vec{d}$  is the permanent electric-dipole moment of the molecules and  $\vec{\mathcal{E}}$  is the electric field of the microwave radiation. To leading order, these electric-dipole transitions are only allowed between different rotational states ( $\Delta N = \pm 1$ ,  $\Delta m_N = \pm 1, 0$ ) while leaving the nuclear spins unchanged [see Fig. 2(a)]. Here,  $N$  is the rotational quantum number and  $m_N$  is the projection of the rotation on the external magnetic-field axis. However, there is a higher order effect due to the interaction between the nuclear electric-quadrupole moments of  $^{40}\text{K}$  and  $^{87}\text{Rb}$  and the electric-field gradient created by the electrons at the nuclear positions. This interaction couples the rotation and the nuclear spins, and allows one to change the hyperfine state of the rovibrational ground-state molecule via two microwave transitions.

In the following, we work with an uncoupled basis set of the form  $|N, m_N, m_I^K, m_I^{\text{Rb}}\rangle$ . For an  $N = 0$  state, the electric-quadrupole interaction vanishes, and ignoring nuclear spin-spin interactions, this basis set corresponds to the hyperfine eigenstates. For rotationally excited states such as  $N = 1$ , the electric-quadrupole interaction mixes quantum states of different hyperfine character with the same sum  $m_N + m_I^{\text{Rb}}$ , which results in eigenstates of the molecular Hamiltonian of the form  $|N = 1, m_N = 0, m_I^K, m_I^{\text{Rb}} \pm 1\rangle + \delta |N = 1, m_N = \pm 1, m_I^K, m_I^{\text{Rb}}\rangle$ , where  $\delta$  typically is small ( $|\delta|^2 \ll 1$ ). (For simplicity, we restrict the discussion here to states relevant for manipulating  $m_I^{\text{Rb}}$ ; however,  $m_I^K$  can be manipulated in a similar manner.) Starting from a particular hyperfine state within the rovibrational ground state,  $|0, 0, m_I^K, m_I^{\text{Rb}}\rangle$ , one can drive a microwave transition to a rotationally excited state with predominantly different hyperfine character, such as  $|1, 0, m_I^K, m_I^{\text{Rb}} \pm 1\rangle$ , therefore changing the nuclear spin of Rb by  $\Delta m_I^{\text{Rb}} = \pm 1$ . The Rabi

frequency of the hyperfine changing transition is then simply given by  $|\delta| \frac{\vec{d} \cdot \vec{\mathcal{E}}}{\hbar}$ . Combining this hyperfine changing microwave transition with a second microwave transition that preserves the nuclear spin and transfers the molecules back into the rotational ground-state manifold ( $|1, 0, m_I^K, m_I^{\text{Rb}} \pm 1\rangle$  to  $|0, 0, m_I^K, m_I^{\text{Rb}} \pm 1\rangle$ ), we can effectively transfer molecular population within the rovibrational ground-state hyperfine manifold [see Fig. 2(b)]. The selection rules for our two-photon transfer scheme are given by  $\Delta m_I^{\text{K/Rb}} = \pm 1$ , and this process can be repeated as needed to prepare the molecules in any hyperfine state within the rovibrational ground-state manifold.

The efficiency of the scheme relies critically on the strength of the mixing of different hyperfine basis states in the rotationally excited state  $N = 1$ . To evaluate the strength of the mixing, we diagonalize the total Hamiltonian  $\mathcal{H}$  of a  $^{40}\text{K}^{87}\text{Rb}$  ( $\nu = 0$ ,  $N$ ) molecule [14] in the uncoupled basis  $|N, m_N, m_I^K, m_I^{\text{Rb}}\rangle$ , in the presence of an external magnetic field of  $B = 545.9$  G, and calculate the 36 (108) eigenvalues and eigenstates of the hyperfine structure within the rotational  $N = 0$  ( $N = 1$ ) manifold. We use the molecular parameters available in the literature [1,6,15]. Experimentally, the mixing of different hyperfine basis states in the rotationally excited state  $N = 1$  can be measured by driving hyperfine changing microwave transitions from  $N = 0$  to  $N = 1$  and comparing the strength of these transitions to the corresponding nuclear spin preserving transitions. Figure 3 shows a comparison between Rabi oscillations for three different microwave transitions: a

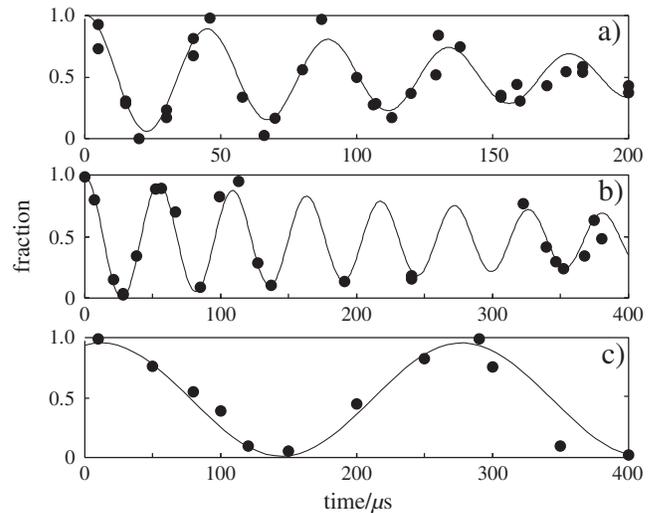


FIG. 3. Rabi oscillations on a (a) hyperfine preserving microwave transition  $|0, 0, -4, 1/2\rangle \rightarrow |1, 1, -4, 1/2\rangle$ ; (b) Rb hyperfine changing transition  $|0, 0, -4, 1/2\rangle \rightarrow |1, 0, -4, 3/2\rangle + \delta |1, 1, -4, 1/2\rangle$ ; (c) K hyperfine changing transition  $|0, 0, -4, 1/2\rangle \rightarrow |1, 0, -3, 1/2\rangle + \delta |1, 1, -4, 1/2\rangle$ . Note the different time axis in panel (a). The microwave power was reduced by a factor of 4 for the data in (a) resulting in an effective decrease of the Rabi frequency by a factor of 2.

TABLE I. Mixing of different hyperfine states in the rotationally excited state  $N = 1$  at  $B = 545.9$  G. We compare the theoretically calculated admixture  $|\delta_{\text{th}}|^2$  to the experimentally measured admixture  $|\delta_{\text{exp}}|^2$ .

Main state	Admixed state	$ \delta_{\text{th}} ^2$	$ \delta_{\text{exp}} ^2$
$ 1, 0, -4, 3/2\rangle$	$ 1, 1, -4, 1/2\rangle$	0.045	$\approx 0.1$
$ 1, 0, -3, 1/2\rangle$	$ 1, 1, -4, 1/2\rangle$	0.0085	$\approx 0.0064$

nuclear spin preserving transition [ $\Delta m_I^{\text{K,Rb}} = 0$ , Fig. 3(a)] and hyperfine changing transitions within the Rb ( $m_I^{\text{Rb}}$ ) and K ( $m_I^{\text{K}}$ ) spin manifold, respectively [Figs. 3(b) and 3(c)].

Table I summarizes the mixing parameter  $|\delta|^2$  for these particular hyperfine state combinations. The mixing between different hyperfine states related to the K nuclear spin is typically  $<1\%$ , whereas it is almost an order of magnitude larger for Rb hyperfine states. This reflects the large quadrupole moment of the Rb nucleus. Note that the above investigated microwave transitions from  $N = 0$  to  $N = 1$  demonstrate spin flips within both the nuclear structure of Rb and K ( $\Delta m_I^{\text{Rb/K}} = \pm 1$ ), which allows the preparation of arbitrary hyperfine states within the rovibrational ground state. Using this scheme, we also demonstrate the preparation of a molecular cloud in the lowest hyperfine state of the rovibrational ground-state manifold characterized by the quantum numbers  $|N = 0, m_N = 0, m_I^{\text{K}} = -4, m_I^{\text{Rb}} = 3/2\rangle$  [see Fig. 1(a)] and find the transfer efficiency within our measurement uncertainty to be unity. An independent theoretical calculation of the microwave spectra of rovibrational ground-state polar  $^{40}\text{K}^{87}\text{Rb}$  molecules is available in [16].

Finally, the experimentally measured one-photon microwave spectrum starting from  $|N = 0, m_N = 0, m_I^{\text{K}} = -4, m_I^{\text{Rb}} = 1/2\rangle$  is fitted to the theoretical calculation of the spectrum. We use the fit for a measurement of three molecular parameters—the rotational constant  $B_e$ , and the electric-quadrupole  $eqQ_{\text{K}}$  and  $eqQ_{\text{Rb}}$  which have previously only been predicted by *ab initio* calculations [6]. Table II summarizes the results. From the best fit, we determine that  $B_e = 1.113950(5)$  GHz,  $eqQ_{\text{K}} = 0.45(6)$  MHz, and  $eqQ_{\text{Rb}} = -1.41(4)$  MHz. Our results are consistent with the *ab initio* calculations in [6], but reduce significantly the uncertainty on the molecular parameters as compared to [6].

To summarize, we have demonstrated the preparation of an ultracold gas of KRb molecules in their absolute lowest energy state—in terms of electronic, vibrational, rotational, and hyperfine degrees of freedom. The demonstrated scheme allows the preparation of arbitrary coherent superpositions of hyperfine states and therefore allows coherent control of molecular population including all quantum degrees of freedom. This paves the way for quantum-state controlled studies of elastic, inelastic, and

TABLE II. Spectrum of rotational transitions from hyperfine state  $|i\rangle$  within  $N = 0$  to hyperfine state  $|j\rangle$  within the  $N = 1$  manifold. We compare the experimentally measured transition frequencies to the theoretical calculation, with the differences listed in the last column. All frequencies are given in kHz. The uncertainties on the transition frequencies are dominated by uncertainty in the external electric field.

State $i$	State $j$	Experiment	Theory	Difference
$ 0, 0, -4, 1/2\rangle$	$ 1, 1, -4, 1/2\rangle$	2 227 837(5)	2 227 835	2
$ 0, 0, -4, 1/2\rangle$	$ 1, 0, -4, 1/2\rangle$	2 228 125(5)	2 228 119	6
$ 0, 0, -4, 1/2\rangle$	$ 1, -1, -4, 1/2\rangle$	2 227 774(7)	2 227 776	2
$ 0, 0, -4, 1/2\rangle$	$ 1, 0, -4, 3/2\rangle$	2 227 009(2)	2 227 008	1
$ 0, 0, -4, 1/2\rangle$	$ 1, -1, -4, 3/2\rangle$	2 227 133(20)	2 227 128	5
$ 0, 0, -4, 1/2\rangle$	$ 1, 0, -3, 1/2\rangle$	2 228 237(10)	2 228 225	12
$ 0, 0, -4, 1/2\rangle$	$ 1, 1, -4, -1/2\rangle$	2 228 588(5)	2 228 593	5
$ 0, 0, -4, 1/2\rangle$	$ 1, 0, -4, -1/2\rangle$	2 228 804(1)	2 228 805	1
$ 0, 0, -4, 3/2\rangle$	$ 1, 0, -4, 3/2\rangle$	2 227 765(10)	2 227 761	4
$ 0, 0, -3, 1/2\rangle$	$ 1, 0, -3, 3/2\rangle$	2 228 109(16)	2 228 091	18

chemically reactive collisions of polar molecules in the ultracold regime.

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