Controlling the hyperfine state of rovibronic ground-state polar molecules

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Ultracold molecules offer entirely new possibilities for the control of quantum processes due to their rich internal structure. Recently, near quantum degenerate gases of molecules have been prepared in their rovibronic ground state. For future experiments, it is crucial to also control their hyperfine state. Here, we report the preparation of a rovibronic ground state molecular quantum gas in a single hyperfine state and in particular in the absolute lowest quantum state. The demonstrated and presented scheme is general for bialkali 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 atomic quantum gases draws much of its success from the unprecedented ability to precisely control the external and internal degrees of freedom of the gas. Control over the external, or motional degree of freedom, comes from realizing ultracold gases in almost arbitrary confining potentials provided by magnetic or optical fields. The internal degrees of freedom, namely the quantum states of the atoms, can be manipulated by driving rf [1] or optical transitions. Because collisional interactions in the gas depend on the internal states, precise control of these quantum states is a prerequisite for creating trapped samples that are stable against inelastic collisions as well as for accessing scattering resonances in order to tune the interparticle interactions [2]. Manipulation of the internal degrees of freedom is also essential in the study of quantum gases, where samples of identical bosons or fermions in a single internal state can behave very differently from spin mixtures. Finally, the precise control of the atomic states is key to quantum information schemes where one seeks to initialize and manipulate atoms as quantum qubits with long coherence times [3].

The precise control of external and internal degrees of freedom will be equally important for the emerging field of ultracold molecular quantum gases. This field has recently seen tremendous progress through the first preparation of near quantum degenerate gas of bialkali molecules in the rovibrational ground state of the electronic ground molecular potential [4, 5]. 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 [6, 7]. However, most molecules will additionally have hyperfine structure within a single rotational and vibrational level [8], and, as is true for ultracold atomic gases, control of these quantum degrees of freedom is essential for future experiments. In particular, for experimental efforts to achieve a Bose-Einstein condensate (BEC) 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. For molecules, an additional possibility is ultracold chemical reactions, whose study will require reliable preparation and detection of the quantum state of the molecules [9]. While previous studies of chemical processes are essentially all done in a temperature range where one has statistical occupation of all hyperfine states, at 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, in the ultracold regime, quantum statistics play a significant role in collisional processes. Control over the nuclear spin of the molecules might even open the door to the study of SU(N) magnetism [10].

Here, we show that we can create ultracold KRb molecules in a single hyperfine state. In addition, we propose and experimentally demonstrate a general scheme for controlling the hyperfine state of bialkali polar molecules in their rovibrational ground state. This scheme allows for the production of ultracold molecules in any arbitrary hyperfine state, and, in particular, is used here to achieve an ultracold gas of KRb molecules all in their absolute lowest energy state (electronic, vibrational, rotational, and hyperfine).

The lowest energy electronic potential for heteronuclear bialkali molecules, such as KRb molecules, is a spin singlet state \( \Sigma^+ \) that has zero electronic angular momentum and spin. Therefore, the hyperfine structure reduces to a nuclear substructure due to 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 \( B = 545.9 \text{G} \) (see below). The \(^{40}\text{K}\) atom has a nuclear spin of \( I^K = 4 \), while \(^{87}\text{Rb}\) has \( I^{Rb} = 3/2 \); together, this gives a total of
Starting from weakly bound $^{40}$K$^{87}$Rb Feshbach molecules formed in the vicinity of a Fano-Feshbach resonance at $B = 546.7$ G [11] [12], 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) [6]. The Raman process bridges an energy gap of $\hbar \cdot 125$ THz. 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 $m_F = -7/2$ [12]. The two Raman laser beams are linearly polarized and co-propagating parallel to the quantization axis defined by the external magnetic field. By conservation of angular momentum, the resulting $X^1\Sigma^+$ ($v = 0, N = 0$) molecules are then restricted to $m_F = m_K^R + m_I^R = -11/2, -7/2, -3/2$ ($\Delta m_F = \pm 2, 0$). Just this consideration leaves 8 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 ($X^1\Sigma^+, v = 0, N = 0$). However, this state is not the lowest energy hyperfine state of the molecule. In the remainder of the paper, we address the question of how to manipulate the hyperfine state of our ground-state polar molecules and, ideally, put them in any one of the 36 possible hyperfine states. In addressing this question, we first prepare molecules in the lowest energy state in Fig. 1(b), which is characterized by $m_K = -4$ and $m_I^R = 1/2$, as a starting point for further manipulation of the hyperfine state.

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 $\frac{d \varepsilon}{\hbar}$, where $d$ is the permanent electric dipole moment of the molecules.
and $\mathbf{E}$ 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 Figure 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 $^{40}$K and $^{87}$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 (driving up to a rotationally excited state and then back down to a different hyperfine ground state).

In the following, we will work with an uncoupled basis set of the form $|N, m_N, m_I^K, m_I^{Rb}\rangle$. 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 $m_N + m_I^{Rb}$, which results in eigenstates of the molecular Hamiltonian of the form $|N = 1, m_N = 0, m_I^K, m_I^{Rb} \pm 1\rangle + \delta |N = 1, m_N = \pm 1, m_I^K, m_I^{Rb}\rangle$. (For simplicity, we restrict the discussion here to states relevant for manipulating $m_I^{Rb}$, however, $m_I^K$ can be manipulated in a similar manner.) Here, the parameter $\delta$ typically is small

$\delta^2 \ll 1$. Starting from a particular hyperfine state within the rovibrational ground state, $|0, 0, m_I^K, m_I^{Rb}\rangle$, one can drive a microwave transition to a rotationally excited state with predominantly different hyperfine character, such as $|1, 0, m_I^K, m_I^{Rb} \pm 1\rangle$, therefore changing the nuclear spin of Rb by $\Delta m_I^{Rb} = \pm 1$. The Rabi frequency of the hyperfine changing transition is then simply given by $|\delta| \frac{E}{\hbar}$. 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 $|1, 0, m_I^K, m_I^{Rb} \pm 1\rangle \rightarrow |0, 0, m_I^K, m_I^{Rb} \pm 1\rangle$, we can effectively transfer molecular population within the rovibrational ground-state hyperfine manifold (see Fig. 2 (b)). The selection rules for the two-photon transfer scheme are then given by $\Delta m_I^{K/Rb} = \pm 1$, 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

\[ |\delta_{exp}|^2 \]

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 $|\delta_{thr}|^2$ to the experimentally measured admixture $|\delta_{exp}|^2$.
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. All frequencies are given in kHz.

| State $i$ | State $j$ | Exp. | Theory | Abs. Diff. |
|-----------|-----------|------|--------|------------|
| $|0 -4 1/2\rangle$ | $|1 -4 1/2\rangle$ | 2227836(5) | 2227835 | 2 |
| $|0 -4 1/2\rangle$ | $|1 0 -4 1/2\rangle$ | 2227836(5) | 2228119 | 6 |
| $|0 -4 1/2\rangle$ | $|1 -1 -4 1/2\rangle$ | 2227774(7) | 2227776 | 2 |
| $|0 -4 1/2\rangle$ | $|1 0 -4 3/2\rangle$ | 2227009(2) | 2227008 | 1 |
| $|0 -4 1/2\rangle$ | $|1 -1 -4 3/2\rangle$ | 2227133(20) | 2227128 | 5 |
| $|0 -4 1/2\rangle$ | $|1 0 -3 1/2\rangle$ | 2228237(10) | 2228225 | 12 |
| $|0 -4 1/2\rangle$ | $|1 1 -4 -1/2\rangle$ | 2228588(5) | 2228593 | 5 |
| $|0 -4 1/2\rangle$ | $|1 0 -4 -1/2\rangle$ | 2228804(1) | 2228805 | 1 |
| $|0 -4 3/2\rangle$ | $|1 0 -4 3/2\rangle$ | 2227765(10) | 2227761 | 4 |
| $|0 -3 1/2\rangle$ | $|1 0 -3 3/2\rangle$ | 2228109(16) | 2228091 | 18 |

The strength of the mixing, we diagonalize the total Hamiltonian $H$ of a $^{40}$K$^{87}$Rb($v = 0, N$) molecule in the uncoupled basis $|N, m_N, m^K, m^Rb\rangle$, in the presence of an external magnetic field $B = 545.9$ 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 [4] [13] [16].

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 nuclear spin preserving transition ($\Delta m^Rb = 0$, see Fig. 3(a)), and hyperfine changing transitions within the Rb ($m^Rb$) and K ($m^K$) spin manifold, respectively (Fig. 3(b) and (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 ($\Delta m^Rb$ and $\Delta m^K$ are almost equal), 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 $|N = 0, m_N = 0, m^K = -4, m^Rb = 3/2\rangle$ (see Fig. I (a)).

An independent theoretical calculation of the microwave spectra of rovibrational ground-state polar $^{40}$K$^{87}$Rb molecules is available in [10].

Finally, the experimentally measured one-photon microwave spectrum starting from $|N = 0, m_N = 0, m^K = -4, m^Rb = 1/2\rangle$ to the rotationally excited manifold $N = 1$ is fitted to the theoretical calculation of the spectrum. We use the fit for a measurement of three molecular parameters - the rotational constant $B$, and the electric-quadrupole $eqQK$ and $eqQRb$ which have previously only been predicted by ab initio calculations [16]. Table II summarizes the results. From the best fit, we determine $B = 1.13950(5)$ GHz, $eqQK = 0.45(6)$ MHz and $eqQRb = -1.41(4)$ MHz. Our results are consistent with the ab initio calculations in [16], but reduce significantly the uncertainty on the molecular parameters as compared to [16].

To summarize, we have demonstrated a general scheme for controlling the hyperfine state of bialkali polar molecules in their rovibrionic ground state. This scheme allows for the production of ultracold bialkali molecules in any arbitrary hyperfine state, and in particular, for the preparation of an ultracold gas of KRb molecules in their absolute lowest energy state (electronic, vibrational, rotational, and hyperfine). This paves the way for quantum-state controlled studies of elastic, inelastic, and chemically reactive collisions of polar molecules in the ultracold regime.

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