Two-photon pathway to ultracold ground state molecules of $^{23}\text{Na}^{40}\text{K}$

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Abstract

We report on high-resolution spectroscopy of ultracold fermionic $^{23}\text{Na}^{40}\text{K}$ Feshbach molecules, and identify a two-photon pathway to the rovibrational singlet ground state via a resonantly mixed $B^1\Pi \sim c^3\Sigma^+$ intermediate state. Photoassociation in a $^{23}\text{Na}^{40}\text{K}$ atomic mixture and one-photon spectroscopy on $^{23}\text{Na}^{40}\text{K}$ Feshbach molecules reveal about 20 vibrational levels of the electronically excited $c^3\Sigma^+$ state. Two of these levels are found to be strongly perturbed by nearby $B^1\Pi$ levels via spin–orbit coupling, resulting in additional lines of dominant singlet character in the perturbed complex $vJX0,01\Sigma^+\rangle \sim \langle vJX0,01\Sigma^+\rangle +$. The dominantly singlet level is used to locate the absolute rovibrational singlet ground state $vJX0,01\Sigma^+\rangle$. We demonstrate coherent two-photon coupling via dark state spectroscopy between the predominantly triplet Feshbach molecular state and the singlet ground state. Its binding energy is measured to be $5212.0447(1)\text{ cm}^{-1}$, a thousand-fold improvement in accuracy compared to previous determinations. In their absolute singlet ground state, $^{23}\text{Na}^{40}\text{K}$ molecules are chemically stable under binary collisions and possess a large electric dipole moment of $2.72\text{ Debye}$. Our work thus paves the way towards the creation of strongly dipolar Fermi gases of NaK molecules.

1. Introduction

Ever since laser cooling and evaporative cooling gave full control over the motional and internal degrees of atoms, there has been a strong effort to extend such control over the richer internal structure of molecules. With large samples of molecules, all occupying the same internal quantum state, controlled switching of chemical reactions could be studied at the quantum level. Their internal degrees of freedom make molecules suitable as potential carriers for quantum information, as a quantum resource for precision measurements and as the building block for novel quantum many-body systems. A particular appeal lies in the creation of new forms of quantum dipolar matter, such as topological superfluids or quantum crystals. The enormous progress towards ultracold molecules over the last decade has been summarized in review papers [1–3], to which one may add the recent successes of magneto-optical trapping [4, 5], a novel type of Sisyphus cooling [6], as well as evaporative cooling of molecules [7], among others. An alternative to direct cooling of molecules, which has so far been limited to temperatures of several millikelvin, is the creation of weakly bound Feshbach molecules at nanokelvin temperatures from a gas of ultracold atoms, which has been achieved for homonuclear [8–14] as well as for heteronuclear molecules [15–22]. Feshbach molecules created out of fermionic atoms were remarkably long-lived [9], allowing the observation of Bose–Einstein condensation [23–28]. However, the dipole moment of such long-range Feshbach molecules is still vanishingly small. In pioneering works at JILA and in Innsbruck, ultracold molecules of fermionic $^{40}\text{K}^{87}\text{Rb}$ and bosonic non-polar $^{133}\text{Cs}_2$ in their absolute rovibrational ground state were created from weakly bound Feshbach molecules via a coherent two-photon transfer [29–31]. $^{40}\text{K}^{87}\text{Rb}$ molecules were found to undergo the reaction $2\text{K}^{87}\text{Rb} \rightarrow \text{K}^{87} + \text{Rb}_2$ [32], precluding further cooling into the deeply degenerate regime. However, confinement to two- and three-dimensional optical lattice potentials allowed to stabilize molecular gases of KRb against reactive collisions [33, 34]. Recently, ultracold gases of bosonic RbCs have been created [35, 36], a molecule that is chemically stable under binary collisions [37].
In the present work we focus on the fermionic molecule $^{23}$Na$^{40}$K, also chemically stable under two-body collisions [37] and known to possess a large electric dipole moment of 2.72 Debye [38], about five times larger than that of KRb. It is therefore an ideal candidate for the formation of a strongly interacting, stable dipolar Fermi gas with interaction energies on the order of tens of percent of the Fermi energy. Following our creation of ultracold Feshbach molecules [20], we here perform one- and two-photon spectroscopy on $^{23}$Na$^{40}$K and identify a two-photon pathway from the predominantly triplet Feshbach molecular state to the absolute rovibrational singlet ground state. A priori, the existence of such a pathway is not obvious, as spin–orbit coupling, mixing singlet and triplet states, is weak for this light molecule.

Historically, NaK was a textbook example of a diatomic molecule and one of the best studied diatomic molecules before the advent of photoassociation (PA) and coherent two-photon spectroscopy of cold and ultracold KRb. The earliest absorption spectra [39] predate modern quantum mechanics, but already within a decade the singlet ground and excited state molecular potentials, and also in

Figure 1. The explored pathway connects the predominantly triplet Feshbach molecular state to a perturbed level of mixed $B''I\Sigma^+$ character via the up-leg laser of frequency $\omega_1$. The states of the three-level system $|F\rangle$, $|E\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential. Excited states $|E\rangle$, $|F\rangle$ and $|G\rangle$ are coupled by up-leg and down-leg lasers with frequencies $\omega_1$, $\omega_2$ and Rabi couplings $\Omega_1$, $\Omega_2$. The transition $|E\rangle \rightarrow |G\rangle$ is associated with the $B''I\Sigma^+$ potential.

The starting point of the experiment is a near degenerate Bose–Fermi mixture of $^{23}$Na–$^{40}$K, as described in our previous work [60]. Since in heatpipe or beam experiments only the deep singlet molecular levels are populated,
the triplet states $c\Sigma^+$ had only been observed where they were strongly perturbed by a nearby $B\Pi$ state. There are thus uncertainties in the exact location of $c\Sigma^+$ energy levels of more than 1 cm$^{-1}. The first task is therefore to perform PA spectroscopy on the atomic ultracold Na–K mixture, as described in section 2. This allows the direct observation of $c\Sigma^+$ levels, and to the ultracold temperatures, only low lying rotational states are accessed. Equipped with the exact locations of the $c\Sigma^+$ levels, and highly accurate predictions on the locations of singlet $B\Pi$ levels from mass-scaled Dunham coefficients for $^{23}$Na$^{40}$K[41, 42], we identify two accidental degeneracies between $c\Sigma^+$ and $B\Pi$ in $^{23}$Na$^{40}$K, namely $B\Pi$ ($|\nu=4\rangle\sim c\Sigma^+\ |\nu=25\rangle$) and $B\Pi$ ($|\nu=12\rangle\sim c\Sigma^+\ |\nu=35\rangle$), where $\nu$ denotes the vibrational quantum number. In section 3 we therefore perform high-resolution spectroscopy on these near-degenerate levels starting with Feshbach molecules. We resolve detailed fine- and hyperfine structure that is well reproduced by our theoretical calculations. The manifold $B\Pi$ ($|\nu=4\rangle\sim c\Sigma^+\ |\nu=25\rangle$) is sufficiently perturbed so that the singlet-dominant feature can be directly addressed from triplet Feshbach molecules. For $B\Pi$ ($|\nu=12\rangle\sim c\Sigma^+\ |\nu=35\rangle$), the observation of two pairs of lines with nearly identical hyperfine structure signals exceptionally strong mixing, originating from an essentially perfect degeneracy and sufficiently strong spin–orbit coupling. Finally in section 4, we perform two-photon spectroscopy, first to locate the absolute rovibrational singlet ground state using Autler–Townes (AT) spectroscopy, then to perform coherent dark state spectroscopy for a high-precision measurement of the binding energy of the rovibrational ground state. The strong singlet–triplet mixing in the intermediate state will enable stimulated rapid adiabatic passage (STIRAP) from Feshbach molecules to absolute singlet ground state molecules. Our work thus opens the door to the creation of a strongly interacting dipolar Fermi gas of $^{23}$Na$^{40}$K molecules.

2. Photoassociation spectroscopy of $^{23}$Na–$^{40}$K

PA spectroscopy is commonly applied to laser-cooled atomic gases trapped in magneto-optical traps (MOTs). However, atomic densities in MOTs are limited to about $10^{11} \text{ cm}^{-3}$, and free-bound transitions to excited molecular levels can typically only reach the long-range part of the excited state potentials. PA in a MOT has additional complications for heteronuclear molecules: the excited state is a strong $C_6$ potential, which has a shorter range than the $C_3$ potential in homonuclear molecules; and overlap of the two MOTs results in severe light-assisted collisions, strongly reducing the effective pair density. Instead of using a MOT, we therefore opted for creating a dense Bose–Fermi mixture of $^{23}$Na–$^{40}$K in an optical trap, cooled close to quantum degeneracy. This allows us to work with atomic densities of up to $10^{12} \text{ cm}^{-3}$. The PA laser can illuminate the atomic sample for several seconds at high laser intensity, revealing even deeply bound lines of the excited state potentials.

To summarize the sequence, as outlined in [20, 60], laser cooled $^{23}$Na and $^{40}$K atoms are first captured in a MOT and optically pumped to the $|f_{\Sigma\Pi}, m_{f\Sigma\Pi}\rangle=[2, 2]$ and $|f_{\Sigma\Pi}, m_{f\Sigma\Pi}\rangle=[9/2, 9/2]$ states before being transferred into an optically plugged magnetic quadrupole trap. In the magnetic trap, the mixture is cooled by forced radiofrequency (rf) evaporation of $^{23}$Na on the $|2, 2\rangle\rightarrow|1, 1\rangle$ transition. $^{40}$K atoms are sympathetically cooled via collisions with $^{23}$Na atoms. At a temperature of about 2 $\mu$K, the mixture is loaded into a crossed optical dipole trap operating at 1064 nm and each species is transferred into the lowest hyperfine states $|1, 1\rangle$ for Na and $|9/2, -9/2\rangle$ for K via Landau–Zener rf sweeps. For the measurements presented in this work, further evaporation in the dipole trap lowers the temperature to about 1 $\mu$K, creating an equal mixture of about $10^5$ atoms of both species close to quantum degeneracy.

PA spectroscopy is performed on the atomic $^{23}$Na–$^{40}$K mixture to explore the electronically excited potentials of $^{23}$Na$^{40}$K (see figure 1). To this end, the near degenerate mixture of Na and K is illuminated with an intense laser beam (laser 1), generated by a tunable continuous wave titanium sapphire laser. The typical peak intensity at the position of the atoms is 7 kW cm$^{-2}$. The polarization of the light is fixed to be diagonal with respect to the vertical magnetic bias field to address both $\pi$ and $\sigma^{\pm}$ transitions to excited states of $^{23}$Na$^{40}$K. In order to efficiently cover a large spectral range during a single experimental run, the frequency of the PA laser is swept while illuminating the ultracold mixture. In general, as we address deeper lying vibrational levels of the electronically excited states, the sweep time is extended to overcome the reduction in Franck–Condor (FC) factors. Typical sweep rates range between 1 and 10 GHz s$^{-1}$. The center positions of the sweeps are recorded using a commercial wavemeter with a spectral resolution of 10 MHz and an absolute accuracy of about 300 MHz.

PA leads to a simultaneous loss of $^{23}$Na and $^{40}$K atoms from the dipole trap. After exposure, PA resonances are located by counting the numbers of remaining Na and K atoms on absorption images of both species. The cycle time for a single set of absorption images is about 30 s.

We investigated electronically excited molecular states in the energy range from 11 900 up to 13 000 cm$^{-1}$, below the atomic $D_1$ transition of $^{40}$K. Figure 2 shows a map of the recorded PA spectra. In order to assign electronic states and vibrational quantum numbers to observed PA transitions, the measured transition frequencies are compared to predictions based on Dunham coefficients for $^{23}$Na$^{40}$K [42, 55, 57] that we mass-scaled for $^{23}$Na$^{40}$K.
We remind here that previous information on the location of triplet energy levels was available only through deperturbation of strongly perturbed levels mixing with singlet states. Errors beyond 1 cm\(^{-1}\) are typical, as we see \textit{a posteriori} from our study. Using an ultracold mixture of unbound atoms, we instead directly access triplet states. Pairs of \(^{23}\text{Na}\) and \(^{40}\text{K}\) atoms in the \(|1, 1\rangle\) and \(|9/2, -9/2\rangle\) states combine into a predominantly ‘stretched’ total spin state \(|F, m_F\rangle = |7/2, -7/2\rangle\). Unbound atom pairs of \(^{23}\text{Na}\) and \(^{40}\text{K}\) thus have a dominant (87.5%) triplet character. Accordingly, most of the observed PA resonances can be assigned to the \(c^3\Sigma^+\) potential. This becomes obvious by comparison to predicted positions of vibrational states of the relevant excited state potentials \(b^3\Pi, c^3\Sigma^+,\) and \(b^3\Pi\) (see figure 2). The \(b^3\Pi\) state is expected to be less visible, as the transition dipole moment between \(a^3\Sigma^+\) and \(b^3\Pi\) vanishes at short-range [61]. From the measured \(c^3\Sigma^+\) energy levels, it will be possible in future work to generate a highly accurate potential energy curve for this electronic state.

The PA spectra allow us to identify two candidate states near 360 and 372.5 THz, in which vibrational levels of the \(b^3\Pi\) and \(c^3\Sigma^+\) potentials are close enough to display significant singlet–triplet mixing (see figure 2). The pairs in question are \(b^3\Pi\left|v = 4\right.\rightarrow c^3\Sigma^+\left|v = 25\right.\) and \(b^3\Pi\left|v = 12\right.\rightarrow c^3\Sigma^+\left|v = 35\right.\). In both cases, accidentally a third electronic state, \(b^3\Pi_\Omega\), intervenes, where the sub-states \(\Omega = 0, 1, 2\) are split by 15 cm\(^{-1}\) [55] due to spin–orbit interaction. Here, \(\Omega\) denotes the total orbital and spin angular momentum projection along the internuclear axis.

For strong two-photon coupling, we require an intermediate state that strongly connects the initial Feshbach molecular state, dominantly associated with the triplet state \(a^3\Sigma^+\left|v = 19, N = 0, J = 1\right.\), to the absolute rovibrational singlet ground state \(X^1\Sigma^+\left|v = 0, J = 0\right.\). Here, \(N\) denotes the quantum number associated with the rotational angular momentum, and \(J\) the total angular momentum neglecting nuclear spins. There are two criteria that need to be fulfilled: first, the intermediate state must feature strong singlet–triplet mixing to mediate coupling between the dominantly triplet Feshbach molecular state and the singlet rovibrational ground state. Second, the intermediate state should have a large transition dipole moment for coupling with both the Feshbach and the absolute ground state. Since the electronic part of the transition dipole moment is fairly constant for both the \(a^3\Sigma^+ ightarrow c^3\Sigma^+\left(\approx 10\right)\) and the \(b^3\Pi ightarrow X^1\Sigma^+\left(\approx 7\right)\) transitions [61], the relevant figure of merit for the second criterion is the FC overlap between the states. Figure 3 shows the calculated FC factors for the transitions from \(a^3\Sigma^+\left|v = 19\right.\) to \(c^3\Sigma^+\) and \(b^3\Pi\) to \(X^1\Sigma^+\left|v = 0\right.\). The FC factors for both candidate states are significant. Note that the typical FC factor for the up-leg transition is two orders of magnitude smaller than for the down-leg transition, indicating that it will be more difficult to achieve substantial coupling between the Feshbach state and the excited state than between the excited state and the absolute ground state.

Regarding the criterion of strong singlet–triplet mixing, spin–orbit matrix elements \(\xi_{bc}\) have been experimentally obtained for \(b^3\Pi \sim c^3\Sigma^+\) with \(^{23}\text{Na}^{39}\text{K}\) [52, 57]. These works consistently found for \(b^3\Pi\left|v = 4\right.\sim c^3\Sigma^+\left|v = 25\right.\) a value of \(\xi_{bc} = 0.16\) cm\(^{-1}\) and for \(b^3\Pi\left|v = 12\right.\sim c^3\Sigma^+\left|v = 35\right.\) \(\xi_{bc} = 0.58\) cm\(^{-1}\). The spin–orbit matrix elements are approximately given by the electronic part of the spin–orbit coupling, which is fairly constant as a function of internuclear distance [57], times the FC overlap between the perturbing states.

**Figure 2.** Photoassociation spectra accessing excited molecular states of \(^{23}\text{Na}^{40}\text{K}\). The observed lines (upper panel) are compared to the prediction of vibrational levels (lower panel) of \(c^3\Sigma^+\) (red), \(b^3\Pi\) (blue), \(b^3\Pi_0\) (green), with lighter colors denoting predictions that lie outside the validity of known Dunham coefficients. Dashed vertical lines indicate the position of resonances that are assigned to the \(c^3\Sigma^+\) potential. The dotted–dashed lines on the right show the \(^{40}\text{K}\) \(D_1\) and \(D_2\) transitions at 12 985.2 and 13 042.9 cm\(^{-1}\), respectively.

\[
\begin{align*}
\text{Photoassociation energy (cm}^{-1}\text{)} & \quad \text{Normalized atom number (a.u.)} \\
12000 & \quad 12200 \\
12400 & \quad 12600 \\
12800 & \quad 13000 \\
\end{align*}
\]

\[
\begin{align*}
\text{Predicted vibrational states} & \quad \text{Photoassociation frequency } \nu J/(2\hbar) \text{ (THz)} \\
360 & \quad 370 \\
380 & \quad 390 \\
\end{align*}
\]
We checked that this overlap does not change significantly between $^{23}\text{Na}^{39}\text{K}$ and $^{23}\text{Na}^{40}\text{K}$. Therefore, these values of $\beta_c \xi$ give an indication how close in energy the singlet and triplet states have to be to undergo significant mixing. In the next section, we investigate the strength of spin–orbit coupling for the candidate states above.

3. Resonantly enhanced singlet–triplet mixing between $B_1\Pi$ and $c_3\Sigma^+$

3.1. Experimental procedure

In order to further investigate the rotational, fine, and hyperfine structure of the two candidate state manifolds, we perform high resolution one-photon spectroscopy on $^{23}\text{Na}^{40}\text{K}$ Feshbach molecules. Working with Feshbach molecules in contrast to free atoms enhances the coupling to the excited states, and deeply bound vibrational levels can be efficiently addressed. Instead of seconds, resonant excitation of Feshbach molecules typically occurs on a time scale of tens of microseconds.

To create Feshbach molecules we use rf association as described in [20]. In short, after preparation of the mixture in the optical dipole trap, $^{40}\text{K}$ atoms are transferred to the $\ket{9/2, -7/2}$ state. Then, a uniform magnetic field of 85.7 G is applied to the atoms, close to a $s$-wave Feshbach resonance in the $\ket{0} = \ket{\text{scattering channel caused by the closed channel molecular state } a^3\Sigma^+ |v = 19\rangle}$, with good or approximate quantum numbers $N = 0, J = 1, F = 9/2$ and $m_F = -7/2$. Here, $F$ is the total molecular angular momentum including the Na and K nuclear spins, and $m_F$ is its projection along the quantization axis. The quantization axis is set by the magnetic field in the vertical direction ($z$-axis). We associate Feshbach molecules by driving the free-bound transition from $\ket{f_{\text{Na}} = 1, m_{\text{Na}} = 1, f_K = 9/2, m_K = -9/2}$ to the molecular state causing the Feshbach resonance in $\ket{f_{\text{Na}} = 1, m_{\text{Na}} = 1, f_K = 9/2, m_K = -7/2}$, with the additional binding energy being provided by the rf photon. At the given magnetic field, we measure the binding energy of the Feshbach molecules to be 80 kHz and convert about 10% of the atoms to yield about $10^7$ Feshbach molecules.

The associated Feshbach molecules are illuminated by laser 1 (see figure 1) to drive transitions to excited states of $^{23}\text{Na}^{40}\text{K}$. Resonant coupling leads to a loss of Feshbach molecules. The intensity of the laser and the exposure time are chosen to clearly reveal the sub-structure of the excited states without saturating the transitions. The laser polarization is fixed to be diagonal with respect to the bias magnetic field. After exposure to the probe laser, an absorption image is taken and the number of remaining Feshbach molecules counted as a function of laser detuning. For absorption imaging, we use light resonant with the $^{40}\text{K}$ atomic transition. Absorption of a first photon breaks the weakly bound Feshbach molecules, followed by scattering of additional photons on the atomic transition.

To achieve high spectral resolution required for precision spectroscopy, the frequency of the probe laser is locked to a high-finesse ultra-low expansion (ULE) cavity in a master-slave configuration. The master laser is directly locked to a transmission mode of the ULE cavity by a Pound–Drever–Hall lock. The probe laser is phase-locked to the master laser with a variable frequency offset. For both lasers, we use home-built grating stabilized
diode lasers. This configuration allows flexible adjustment of the probe laser detuning over a range of 10 GHz with kHz precision. The cavity has a finesse of $\sim 35\,000$ near 360.2 THz (832.2 nm), and $\sim 15\,000$ near 372.6 THz (804.7 nm), suitable for addressing both candidate states. The temperature of the cavity is stabilized for long term frequency stability. Absolute frequency determination is performed for the most part with the help of a commercial wavemeter of 300 MHz accuracy as described above. One particular single-photon transition is determined to 3 MHz accuracy using a frequency comb, as discussed below.

3.2. Analysis of the fine structure

Figures 4 and 5 show the observed fine (a) and hyperfine (b)–(e) structure of the two state manifolds at 360 and 372 THz, respectively. In order to understand the spectral structure, we analyze the perturbations among nearly degenerate electronically excited states, following the approach of [53]. As a result of the theoretical analysis presented here, we are able to reproduce the observed fine and hyperfine structure, to characterize the electronic state decomposition, and to assign angular momentum quantum numbers.

The fine structures of the 360 and 372 THz manifolds in figures 4(a) and 5(a) show nine and eight significant loss features, respectively. The state diagram of figure 6 illustrates the various molecular states that are involved in the fine structure. Starting with triplet Feshbach molecules in the lowest rotational state $N = 0, J = 1$ of positive parity, only electronically excited states with negative parity and $J = 0, J = 1$ or $J = 2$ can be reached. The $c^{3}\Sigma^{+}$ electronic state, being close to Hund’s case (b), offers four such states: $|N = 1, J = 0, 1, 2\rangle$ and $|N = 3, J = 2\rangle$, where the latter is coupled to $|N = 1, J = 2\rangle$ via spin–spin coupling (vertical dotted line in figure 6). The $B^{1}\Pi$ electronic state contributes two states, the $e$ state with $J = 1$ and the $f$ state with $J = 2$. The remaining three (360 THz manifold) and two (372 THz manifold) features are associated with the $b^{3}\Pi_{0}$ electronic state, introducing three states with $J = 0, J = 1, J = 2$. As negative parity states are involved in the excited state, odd $J$ corresponds to $e$ symmetry and even $J$ to $f$ symmetry. The $e/f$ label will be omitted in the following discussion.

The fine structure around 360 THz is associated with the perturbed complex $B^{1}\Pi|v = 4\rangle \sim c^{3}\Sigma^{+} |v = 25\rangle \sim b^{3}\Pi_{0}|v = 59\rangle$, while the 372 THz manifold is caused by $B^{1}\Pi|v = 12\rangle \sim c^{3}\Sigma^{+}|v = 35\rangle \sim b^{3}\Pi_{0}|v = 66\rangle$. For clarity of this presentation, we neglect the influence of the other $b^{3}\Pi_{1,2}$ states that are far off-resonant, a distance of 15 and 30 cm$^{-1}$ higher in energy [55]. However, they are included in the calculations that reproduce the observed spectra, where they cause minor shifts of lines.

The Hamiltonian governing the fine structure of the perturbed $B \sim c \sim b$ complex is [53, 54, 62]

$$H_{\text{fine}} = H_{B}^{\text{B}} + H_{S}^{\text{S}} + H_{SK}^{\text{SK}} + H_{\text{SO}}^{\text{SO}} + H_{BC}^{\text{BC}} + H_{BC}^{\text{BC}}.$$  \hspace{1cm} (1)

The deperturbed energy levels $E_{B,c,b}$ of electronic states and their rotational energies (with rotational constants $B_{B,c,b}$) are included in $H_{B,c,b}^{\text{B}}$. $E_{S}$ and $E_{c}$ are taken to be the deperturbed energies in the absence of spin–orbit coupling of $B^{1}\Pi$ ($J = 1$) and $c^{3}\Sigma^{+}$ ($|N = 1, J = 1\rangle$, respectively. $E_{B}$ is the deperturbed energy of the $b^{3}\Pi_{0}$ ($J = 0$) state. Within $c^{3}\Sigma^{+}$, we include spin–spin coupling $H_{SK}$ with coupling constant $\lambda$, and the weak spin–rotation coupling $H_{\text{SO}}$ with constant $\gamma$, which is diagonal in the chosen Hund’s case (b) basis. The couplings are schematically shown in figure 6. States $B^{1}\Pi$ and $c^{3}\Sigma^{+}$ are connected via spin–orbit coupling $H_{\text{SO}}^{\text{SO}}$ (coupling constant $\xi_{bc}$). Also the electronic states $b^{3}\Pi_{0}$ and $c^{3}\Sigma^{+}$ are coupled via spin–orbit coupling $H_{\text{SO}}^{\text{SO}}$ (coupling constant $\xi_{bc}$), and in addition, for $J \neq 0$, via weak $L$-uncoupling $H_{\text{BC}}^{\text{BC}}$ (coupling constant $\xi_{bc}$). The latter has a minute influence for the low rotational states considered here, and will be neglected in the discussion, but is included in the calculation.

All of the above perturbations conserve total angular momentum $J$, so that the full Hamiltonian can be broken down into sub–Hamiltonians that only act within sub–spaces with fixed $J$. In the basis $\{c^{3}\Sigma^{+} |N = 1, J = 0\rangle, b^{3}\Pi_{0} |J = 0\rangle\}$, the Hamiltonian for $J = 0$ is

$$H_{J=0} = \begin{pmatrix}
E_{c} - 2\lambda & -\sqrt{2}/2 \xi_{bc} \\
-\sqrt{2}/2 \xi_{bc} & E_{B}
\end{pmatrix}.$$  \hspace{1cm} (2)

For $J = 1$, neglecting $L$-uncoupling, another $2 \times 2$ matrix connects the states in the basis $\{B^{1}\Pi |J = 1\rangle, c^{3}\Sigma^{+} |N = 1, J = 1\rangle\}$ via spin–orbit coupling

$$H_{J=1} = \begin{pmatrix}
E_{B} & \xi_{bc} \\
\xi_{bc} & E_{c}
\end{pmatrix}.$$  \hspace{1cm} (3)

$L$-uncoupling causes weak coupling of $c^{3}\Sigma^{+} |N = 1, J = 1\rangle$ to $b^{3}\Pi_{0} |J = 1\rangle$, which is responsible for the extremely weak and narrow $J = 1$ feature near 360.162 THz in figure 4(a). The corresponding feature in the 372 THz manifold was not found, presumably due to even weaker $L$-uncoupling. Finally, the $J = 2$ sub-space is governed by a $4 \times 4$ matrix in the basis $\{B^{1}\Pi |J = 2\rangle, c^{3}\Sigma^{+} |N = 1, J = 2\rangle, c^{3}\Sigma^{+} |N = 3, J = 2\rangle, b^{3}\Pi_{0} |J = 2\rangle\}$, neglecting influence of far off-resonant states $b^{3}\Pi_{1,2}$.
As a starting point for the analysis of the spectra, we use deperturbed energy levels and rotational constants, obtained by mass-scaling of existing $^{23}$Na $^{39}$K data on $B'\Pi$ [41], $c'\Sigma^+$ [52, 57] and $b'\Pi_0$ [52, 55, 57] states.
b^1Π_u^\varphi | v = 66 \rangle \) has not been observed before and falls outside the validity of the Dunham expansion given in \[57\].

The above perturbations shift the energy levels, and the corresponding coupling constants serve as variables to match the theory with the experimental data. An initial estimate of $a \approx 0.58 \text{ cm}^{-1}$ for the 360 THz manifold and $0.16 \text{ cm}^{-1}$ for the 372 THz manifold was discussed in the previous section \[57\]. The value of $\delta_{bc} = 0.77$ for the 360 THz manifold is obtained from measured values in \[57\] after weighting with the proper FC factors.

Values of $\gamma$ and $\beta_\lambda$ for $^{23}\text{Na}^{39}\text{K}$ can be found in \[52\] and serve as initial values here. By varying the spin–spin coupling constant $\lambda$ of $c^3\Sigma^+$, the unknown spin–orbit coupling $\delta_{bc}$ of the 372 THz manifold, and the deperturbed energy levels $E_{b,c,h}$, excellent agreement with the observed fine and hyperfine structure is obtained (see figures 4 and 5).

The $J$ quantum numbers of the observed fine structure features are identified by considering their distinct hyperfine and Zeeman sub-structure. The two $J = 0$ states are featureless, and $J = 1$ and $J = 2$ states show characteristic patterns, to be analyzed below. For either of the two manifolds, strong $b \sim c$ spin–orbit coupling explains the unusual presence of a $J = 0$ state in the midst of states with higher $J$.

For the present task of finding a two-photon pathway from Feshbach molecules to the absolute singlet ground state, the $J = 1$ states are highly relevant. In the 360 THz manifold (see figure 4(a)) the two $J = 1$
features are well separated by 1 cm\(^{-1}\). This is significantly larger than the expected strength of spin–orbit coupling for these states given the initial estimate of \(\xi_{\text{BC}} = 0.16\) cm\(^{-1}\) (our analysis yields 0.27 cm\(^{-1}\), see below). Thus the states are relatively weakly mixed. As a consequence, the high resolution scans of the two \(J = 1\) features in figure 4(b) and (d) show weak resemblance in their structure. Nevertheless, the very fact that two \(J = 1\) features are observable is a consequence of spin–orbit coupling, because a purely singlet state would not be detectable in our scans. The analysis reveals that state (b) has 92% triplet character, and therefore displays a Zeeman triplet of energy levels with magnetic quantum numbers \(m_J = -1, 0, +1\).

In stark contrast, the 372 THz manifold (see figure 5(a)) contains two pairs of states, two \(J = 1\) states ((b) and (d)) and two \(J = 2\) states ((c) and (e)), whose respective hyperfine structure is nearly identical. This 'line doubling' of an apparent \(c^3\Sigma^+\) state is well-known from previous spectroscopic studies of NaK \([41, 49–53]\), and it results from strong mixing of \(c^3\Sigma^+\) with \(B'\Pi\). The energy difference between the two \(J = 1\) features is about 1.23 cm\(^{-1}\), comparable to twice the spin–orbit matrix element \(\xi_{\text{BC}} = 0.58\). As the \(J = 1\) states can approximately be considered to form a two-level system (see \(H_{\text{fine}}\) above), we can write each of them as a superposition:

\[
|J = 1\rangle_{(b)} = \alpha \left| c^3\Sigma^+, N = 1, J = 1 \right\rangle + \beta \left| B'\Pi, J = 1 \right\rangle,
\]

\[
|J = 1\rangle_{(d)} = -\beta^* \left| c^3\Sigma^+, N = 1, J = 1 \right\rangle + \alpha^* \left| B'\Pi, J = 1 \right\rangle.
\]

As the hyperfine structure is largely dominated by the \(c^3\Sigma^+\) contribution, the ratio of the widths of the hyperfine features reveals the value of \(|\alpha|^2/|\beta|^2 \approx 1.6\). The full perturbation analysis including hyperfine and Zeeman structure gives \(|\alpha|^2/|\beta|^2 = 1.8\), implying \(\alpha = 0.80\) and \(\beta = 0.60\). We thus have identified a pair of states with a nearly even, 64%–36% mixing between singlet and triplet states.

### 3.3. Analysis of the hyperfine structure

To understand the hyperfine and Zeeman structures found in the high-resolution scans of figures 4(b)–(e) and figures 5(b)–(e), we include in the total Hamiltonian the Zeeman interaction of states \(B'\Pi\) and \(c^3\Sigma^+\) \((H_{z, \text{K}})\) and the hyperfine interaction within \(c^3\Sigma^+\), consisting of the Fermi contact interaction of the electronic spin with the sodium and the potassium nucleus \((H_{\text{hf, Na}} \text{ and } H_{\text{hf, K}})\) as described in [53]

\[
H_{\text{total}} = H_{\text{fine}} + H_{\text{hf, Na}} + H_{\text{hf, K}} + H_{z, \text{K}}.
\]

The Zeeman Hamiltonian for the \(B'\Pi\) state is [62]

\[
H_{z, B} = \mu_B L_z B,
\]

where \(\mu_B\) is the Bohr magneton and \(L_z\) the \(z\)-component of the molecule's orbital angular momentum in the laboratory frame. \(H_{z, B}\) is diagonal in the \(|J_m\rangle\) basis of rotational states of \(B'\Pi\) with matrix elements.
\[
\langle m_J | H^\parallel | m_J \rangle = \mu_B B \frac{m_J}{J(J+1)},
\]

(4)

describing the projection of the one unit of angular momentum along the internuclear axis onto the magnetic field in the laboratory z-axis; \(m_J\) denotes the z-projection of \(\vec{J}\). In particular, the magnetic moment of a \(J = 1, m_J = 1\) state is \(\mu_J = \frac{2}{\hbar}\), causing a Zeeman splitting of about 60 MHz, close to what we observe for the dominantly \(B'\Sigma^+\) state in figure 4(d). Additional splitting and broadening is due to the admixture of \(c'^3\Sigma^+\), which introduces hyperfine and additional Zeeman shifts. For the \(c'^3\Sigma^+\) state, the Zeeman term is

\[
H^Z = \mu_B g_S S_z
\]

with \(S_z\) the z-component of the electron spin the laboratory frame, and \(g_S\) its g-factor. Note that \(H^Z_2\) is not diagonal in the Hund’s case (b) basis, which mixes states of differing spin projection along the internuclear axis [62, 63]. The hyperfine Hamiltonians are

\[
H^Z_{\text{Na}} = \alpha_{\text{Na}} \vec{I}_{\text{Na}} \cdot \vec{S} \quad \text{and} \quad H^Z_{\text{K}} = \alpha_{\text{K}} \vec{I}_{\text{K}} \cdot \vec{S},
\]

where \(I_{\text{Na}}\) and \(I_{\text{K}}\) denote the nuclear spin for \(^{23}\text{Na}\) and \(^{40}\text{K}\), respectively. A major simplification of the analysis is afforded by the large splitting between states of different \(J\), compared to the hyperfine (and Zeeman) splitting \((\alpha_{\text{Na}} \approx 300 \text{ MHz} \text{ and } \alpha_{\text{K}} \approx 30 \text{ MHz}). Therefore remains a good quantum number.

The dominant contribution of the hyperfine interaction in \(c'^3\Sigma^+\) originates from the \(^{23}\text{Na}\) nucleus, which has a nuclear spin \(I_{\text{Na}} = 3/2\). This leads to three (four) hyperfine manifolds for \(J = 1 (J = 2)\) at zero field, labelled by the quantum number \(F_1\), corresponding to the addition of the sodium nuclear spin to the total angular momentum \(\vec{J}\) excluding nuclear spins, \(\vec{F}_1 = \vec{J} + \vec{I}_{\text{Na}}\). For \(J = 1\) possible values are \(F_1 = 1/2, 3/2\); and \(5/2, 7/2\); for \(J = 2\) additionally \(F_1 = 7/2\) occurs. The appropriate hyperfine constants for various vibrational levels of \(c'^3\Sigma^+\), including the ones relevant here \((|v| = 25\text{ and } |v| = 35\)) were measured in [41, 52, 53] for \(^{23}\text{Na}\)-\(^{39}\text{K}\). To include the hyperfine interaction of electron spins with the potassium nucleus [53] one introduces the total angular momentum \(\vec{F} = \vec{F}_1 + \vec{I}_{\text{K}} = \vec{J} + \vec{I}_{\text{Na}} + \vec{I}_{\text{K}}\), with \(I_{\text{K}} = 4\), causing new levels to appear from each \(F_1\) level (for example, \(F_1 = 1/2\) leads to \(F = 7/2\) and \(F = 9/2\)). Finally, the Zeeman interaction at 85.7 G further splits these lines. The only remaining strictly ‘good’ quantum number is the z-component of the total angular momentum, \(m_f\). Still, for well-separated levels, \(F_1\) and the z-component of \(m_f\) are often approximately defined.

In order to understand the observed hyperfine spectra, we analyze which states are accessible starting from the initial Feshbach molecular state with \(m_f = -7/2\). Possible final states that can be reached via diagonal polarization are \(m_f = -5/2, -7/2, -9/2\). An additional approximate selection rule comes from the fact that the closed-channel Feshbach molecular state is predominantly in the total angular momentum state \(F = 9/2\), the open-channel is in \(F = 7/2\), so that transitions to excited states \(F = 13/2\) or \(F = 3/2\) are forbidden. Working in the nuclear spin–decoupled basis of \(|N, J, m_J, I_{\text{Na}}, I_{\text{K}}, m_{f_{\text{Na}}}, m_{f_{\text{K}}}\rangle\) for \(c'^3\Sigma^+\), and noticing that the Feshbach molecules have \(|N = 0, J = 1\rangle\,\text{, the line strength is described by the Hönbl–London factor } \frac{2J + 1}{2J - 1}\langle m_J | 1 \: p | m_J \rangle^2.\) The symbol in brackets denotes a Clebsch–Gordan matrix element, and \(p\) describes the laser polarization, where \(p = 0\) stands for linear, and \(p = \pm 1\) for \(\sigma^\pm\) circularly polarized light. The calculated spectra are shown above the measured data in figure 4(b)–(e) and figure 5(b)–(e). They reproduce the observed line structure well. Most lines consist of several individual hyperfine components, indicated by individual lines within the theoretical spectrum. Table 1 summarizes the parameters used to reproduce the observed spectra.

We can compare our results for the hyperfine constants with the literature on \(^{23}\text{Na}_{\text{39K}}\). For \(c'^3\Sigma^+\) \(|v = 25\rangle\) and \(|v = 35\rangle\) [52], found \(\alpha_{\text{Na}} = 312 (6) \text{ MHz}\) (in agreement with [53]) and 342 (6) MHz, respectively. For \(^{23}\text{Na}_{\text{40K}}\), our analysis yields \(\alpha_{\text{Na}} = 334 (4) \text{ MHz}\) for \(|v = 25\rangle\) and \(\alpha_{\text{Na}} = 342 (2) \text{ MHz}\) for \(|v = 35\rangle\), the latter in excellent agreement with the work on \(^{23}\text{Na}_{\text{39K}}\) [52]. The influence of the potassium nucleus on the hyperfine structure had previously either not been observed [52] or only indirectly through broadening of Na-dominated hyperfine lines [53], leading to estimates \(\alpha_{\text{K}} < 10\text{ and 18 MHz},\) respectively. From the known atomic hyperfine constant, the probability for finding an s-electron near the \(\text{K}^{39}\) nucleus was estimated to be 15% [53].

For \(\text{K}^{40}\), this would yield \(\alpha_{\text{K}} = -22 \text{ MHz}\); note the negative sign due to the anomalous sign of the \(\text{g}\)-factor of the \(\text{K}^{40}\) nucleus. Here, we find \(\alpha_{\text{K}} = -37 (4) \text{ MHz}\) for \(|v = 25\rangle\) and \(\alpha_{\text{K}} = -28 (4) \text{ MHz}\) for \(|v = 35\rangle\).

To summarize, we identified promising intermediate states for two-photon coupling of Feshbach molecules to the absolute singlet ground state. In the next section we demonstrate this coupling directly. We first determine the previously uncertain location of the ground state via AT spectroscopy and then perform coherent dark state spectroscopy for a precise measurement of the binding energy.

4. Ground state spectroscopy of \(^{23}\text{Na}_{\text{40K}}\)

Before our study, the latest value on the position of the absolute rovibrational ground state of bosonic \(^{23}\text{Na}_{\text{39K}}\), relative to the dissociation limit of unbound atoms, was 5211.75 (10) \text{ cm}^{-1} [44]. The relatively small error bar is
a testament to the long history of high-resolution laser spectroscopy on NaK. For conventional heatpipe or molecular beam experiments, the main challenge is to precisely pin-point the dissociation energy, as the most weakly bound state of the triplet potential had not been directly observed. Working with Feshbach molecules, associated from free atoms, overcomes this problem. The measurement of interspecies Feshbach resonances between $^{23}$Na and $^{40}$K fixed the position of the weakest bound state relative to the dissociation energy [20, 60]. Precise knowledge of the long-range van der Waals forces then allows in principle to assign absolute values to the binding energy of previously observed energy levels.

Our observation of the singlet-rich feature in the $B'II$ ($v = 4$) $\sim c^3\Sigma^+$ ($v = 25$) $\sim b^1\Pi$ ($v = 59$) (see figure 4(d)) allows for a direct measurement of the singlet rovibrational ground state binding energy using twophoton spectroscopy. The dominant spin singlet character of this state results in strong coupling to the singlet ground state, which in turn induces a large AT splitting of the excited state.

For conducting two-photon spectroscopy, similar to the experimental procedure of the previous section, we first prepare an ultracold gas of $^{23}$Na-$^{40}$K Feshbach molecules in a crossed optical dipole trap. Then, the molecules are simultaneously exposed to a weak up-leg laser 1 resonantly addressing the singlet dominated $J = 1$ state of the $B'II$ ($v = 4$) $\sim c^3\Sigma^+$ ($v = 25$) branch, and a strong down-leg laser 2 coupling the $X'\Sigma^+$ ($v = 0$, $J = 0$) state to this intermediate state (see figure 1). After a set exposure time, an absorption image of the remaining Feshbach molecules is taken by imaging the $^{40}$K component of the molecules. The number of remaining Feshbach molecules is recorded as a function of the down-leg laser detuning.

In the absence of the down-leg light, the up-leg laser would simply remove most Feshbach molecules from the trap by exciting the molecules to the intermediate state. However, when the down-leg laser is strong and sufficiently close to resonance, it shifts the excited state via the AC Stark effect by more than a linewidth, thereby ‘protecting’ Feshbach molecules from loss. This gives the criterion for the width of the protection window: the AC Stark shift $\Omega_2 / 2\delta_2$ due to the down-leg coupling laser at detuning $\delta_2$ needs to exceed the linewidth $\Gamma$ of the excited state, so the detuning should not exceed $\Delta_2 / \Gamma$. If the down-leg Rabi frequency is significantly larger than the excited state linewidth, it opens up a wide protection window, facilitating the observation of the singlet ground state. In this so-called AT regime, the protection of Feshbach molecules against loss originates from two-level interaction between the intermediate state and the target rovibrational ground state, and requirements on phase coherence between the two Raman lasers are relaxed.

A starting point for the study, the binding energy of the rovibrational ground state of $^{23}$Na-$^{40}$K is obtained via mass-scaling the best value for $^{23}$Na-$^{39}$K. For the chosen intermediate state, the resonant down-leg frequency lies around 516 THz, corresponding to 580 nm, in the visible range. For generating this wavelength, we use a continuous wave dye laser operating with Rhodamine 6 G dye. The broad tunability of a dye laser together with a large output power of $>1$ W has been instrumental in locating the rovibrational ground state.

In figure 7(a), the normalized Feshbach molecule number after exposure to the Raman lasers is plotted as a function of the down-leg laser detuning. As the laser frequency is tuned close to the energy difference between the intermediate state and the rovibrational ground state, we observe a large window of AT protection of about 1.3 GHz. This signals the observation of the absolute ground state. The width of the protection window was on the order of the uncertainty in the ground state binding energy, facilitating the observation of the ground state.

To accurately measure the AT splitting and determine the down-leg Rabi coupling $\Omega_2$, we fix the down-leg laser to be on resonance between the intermediate state and the rovibrational ground state and scan the up-leg

---

**Table 1.** Molecular constants and interaction parameters for the two resonant $B'II \sim c^3\Sigma^+ \sim b^1\Pi_b$ manifolds. Calculated line positions of the fine structure agree with the experimental data to within the experimental accuracy of about 300 MHz, dominated by wavemeter error. The deperturbed energies $E_{b,c}$, are given with respect to the bottom of the $X'\Sigma^+$ ground state potential. All values are in units of cm$^{-1}$.

| Parameter | $B'II$ ($v = 4$) $\sim c^3\Sigma^+$ ($v = 25$) $\sim b^1\Pi$ ($v = 59$) | $B'II$ ($v = 12$) $\sim c^3\Sigma^+$ ($v = 35$) $\sim b^1\Pi$ ($v = 66$) |
|-----------|-------------------------------------------------|-------------------------------------------------|
| $E_b$     | 17 289.158                                      | 17 701.427                                      |
| $E_c$     | 17 288.338                                      | 17 701.074                                      |
| $E_b$     | 17 287.308                                      | 17 699.680                                      |
| $B_b$     | 0.0062                                          | 0.0551                                          |
| $B_c$     | 0.00461                                         | 0.0392                                          |
| $B_b$     | 0.0024                                          | 0.0540                                          |
| $\delta_b$ | 0.27                                           | $0.5899 \ (J = 1), 0.5833 \ (J = 2)$           |
| $\delta_c$ | 0.766                                          | 0.68                                            |
| $\lambda$ | $-0.174$                                        | $-0.55$                                         |
| $\gamma$  | 0.0022                                          | 0.0215                                          |
| $\beta_b$ | 0.0035                                          | 0.006                                           |
| $\alpha_{Na}$ | 0.0112                                         | 0.0114                                          |
| $\alpha_{K}$ | $-1.2 \times 10^{-3}$                         | $-0.94 \times 10^{-3}$                         |
laser frequency. In Figure 7 (b), the normalized number of remaining Feshbach molecules is plotted as a function of the up-leg detuning. From the measured splitting and known beam parameters, we obtain a normalized down-leg Rabi frequency of $\bar{\Omega} = 40(10) \times 10^3$ kHz, indicating strong coupling.

With the rovibrational ground state located, we accurately measure the binding energy of the $v\Sigma X = 0, 01\Sigma$ state via coherent dark state spectroscopy. In the limit of weak down-leg Rabi coupling, the transition probability to excite Feshbach molecules into the intermediate state is coherently canceled when the Raman lasers satisfy the two-photon resonance condition. In contrast to AT protection, the protection of Feshbach molecules is now due to electromagnetically induced transparency (EIT) [64], which relies on the relative phase coherence between the two Raman lasers.

The Raman laser coherence is maintained by locking both lasers 1 and 2 to a common ULE cavity using the Pound–Drever–Hall technique. The cavity is coated for a finesse of $\sim 35 000$ in the vicinity of the up-leg and the down-leg transitions, and has a free spectral range of 1.5 GHz. For providing fast frequency feedback to the coupling dye laser, an electro-optic modulator is inserted into the laser cavity and driven by a high bandwidth amplifier. Frequency tuning of the dye laser is achieved with an external acousto-optic modulator. As in the previous section, for addressing the up-leg transition, we use two grating stabilized diode lasers in a master-slave configuration.

In Figures 8(a) and (b), we show the observed dark state resonance lineshapes, using the 360 THz singlet dominated $J = 1$ feature in Figure 4(d), as well as the lower $J = 1$ feature of the 372 THz manifold in Figure 5(b), respectively. For detection, we record the number of remaining Feshbach molecules after exposure to the Raman lasers as a function of the up-leg detuning. The down-leg laser is fixed to be on resonance. The observed lineshapes are fitted by a simplified three-level master equation model, which takes the down-leg Rabi frequency as a free parameter. For convenient absolute calibration of the down-leg frequency $\omega_2$, we employ iodine spectroscopy and reference to the iodine atlas [66], cross-checked with the program Iodine Spec [67]. The frequency difference between the intermediate state feature of Figure 4(d) and the rovibrational ground state was measured to be $\omega_2 = 2 \pi \times 516.472 613(3)$ THz, accurate to the MHz-level. The corresponding up-leg frequency $\omega_1 = 2 \pi \times 360.221 309(1)$ THz was calibrated using an optical frequency comb. We obtain a
binding energy of $D_0^{(X)} = 5212.0447(1) \text{ cm}^{-1}$ for the rovibrational singlet ground state of $^{23}\text{Na}^{40}\text{K}$, relative to the dissociation threshold and the hyperfine center of mass of the constituent atoms. Adding the zero-point energy $61.5710 \text{ cm}^{-1}$, the depth of the $X_1^1\Sigma^+$ ground state potential is $D_e^{(X)} = 5273.6157 \text{ cm}^{-1}$. This corresponds to a thousand-fold reduction in the uncertainty compared to previous determinations [44].

5. Conclusion

In this work, we have identified a suitable pathway towards the production of ultracold ground state molecules of fermionic $^{23}\text{Na}^{40}\text{K}$, starting with Feshbach associated pairs of ultracold atoms. One-photon spectroscopy directly revealed the $c^3\Sigma^+$ triplet state of NaK, whose levels had only been observed before in the presence of strong perturbation by nearby singlet states. We identified two strongly perturbed $c^3\Sigma^+ \sim b^3\Pi \sim b^1\Pi_0$ manifolds in $^{23}\text{Na}^{40}\text{K}$, which feature levels of strongly mixed singlet and triplet character. Hyperfine-resolved spectroscopy revealed in one case almost equal singlet–triplet mixing. These excited energy levels were shown to be ideal stepping stones for a two-photon process that connects the weakly bound Feshbach molecular state to the $X^1\Sigma^+ |v=0, J=0\rangle$ absolute rovibrational singlet ground state. We performed Autler-Townes spectroscopy to detect the absolute ground state, and demonstrated coherent two-photon dark state spectroscopy for a precision measurement of the singlet ground state binding energy. The two resonantly mixed excited state manifolds should allow an efficient STIRAP from Feshbach molecules to absolute singlet ground state molecules. In this ground state, $^{23}\text{Na}^{40}\text{K}$ molecules are chemically stable against binary collisions [37] and possess a large induced electric dipole moment of 2.72 Debye. The results presented here pave the way towards the creation of a strongly interacting dipolar Fermi gas of chemically stable NaK molecules [68].

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