Hyperfine, rotational, and vibrational structure of the $a^3\Sigma^+_u$ state of $^{87}\text{Rb}_2$

C. Strauss $^1$, T. Takekoshi $^1$, F. Lang $^1$, K. Winkler $^1$, R. Grimm $^1$, and J. Hecker Denschlag $^{1,2}$

$^1$Institut für Experimentalphysik und Zentrum für Quantenphysik, Universität Innsbruck, 6020 Innsbruck, Austria

$^2$Institut für Quantenmaterie, Universität Ulm, 89069 Ulm, Germany

E. Tiemann $^3$

$^3$Institute of Quantum Optics, Leibniz Universität Hannover, 30167 Hannover, Germany

(Dated: October 15, 2010)

We have performed high-resolution two-photon dark-state spectroscopy of an ultracold gas of $^{87}\text{Rb}_2$ molecules in the $a^3\Sigma^+_u$ state at a magnetic field of about 1000 G. The vibrational ladder as well as the hyperfine and low-lying rotational structure is mapped out. Energy shifts in the spectrum are observed due to singlet-triplet mixing at binding energies as deep as a few hundred GHz$\times h$. This information together with data from other sources is used to optimize the potentials of the $a^3\Sigma^+_u$ and $X^1\Sigma^+_g$ states in a coupled-channel model. We find that the hyperfine structure depends weakly on the vibrational level. This provides a possible explanation for inaccuracies in recent Feshbach resonance calculations.

PACS numbers: 42.62.FI, 33.20.-t, 37.10.Mn

I. INTRODUCTION

Recently, optical schemes have been developed to selectively produce cold and dense samples of deeply bound molecules in well defined quantum states [1–3] (see also [4, 5]). This has opened up new possibilities for cold collision experiments, ultracold chemistry [6–8], and for testing fundamental laws via precision spectroscopy [9–11]. For such future experiments it is mandatory that the location and properties of the available molecular quantum states are well known and understood.

Until recently, the $a^3\Sigma^+_u$ triplet potential of the $\text{Rb}_2$ molecule has remained largely experimentally unexplored. Natural samples of $\text{Rb}_2$ are normally found in their $X^1\Sigma^+_g$ singlet state from which the lowest triplet state is sufficiently difficult to reach in an optical Raman process due to a change in $u/g$ symmetry. Here we report precision spectroscopy of $^{87}\text{Rb}_2$ molecules in this lowest triplet state, $a^3\Sigma^+_u$ ($5S_{1/2} + 5S_{1/2}$), where we resolve vibrational, rotational, hyperfine and Zeeman structure with an accuracy as high as 30 MHz. We use dark-state spectroscopy where a gas of weakly bound Feshbach molecules is irradiated by two laser beams. Molecular losses, induced by one of the two lasers, are suppressed when the second laser is tuned into resonance with a bound state (see Fig. 1). Fitting a coupled-channel model to our experimental data, we have constructed an accurate Born-Oppenheimer potential for $a^3\Sigma^+_u$. This enables us to calculate the wave functions of triplet bound states as well as their binding energies to 60 MHz$\times h$ accuracy (where $h$ is Planck’s constant) over the whole manifold of vibrational and low rotational ($N<5$) levels. Our theory and data agree to the extent that further refinement of the theoretical model requires a reduction in the experimental uncertainty.

Molecular spectroscopy with cold atomic gases goes back to the beginnings of laser cooling [12, 13]. An experiment closely related to ours is the one by Araujo et al. [15] where the Na$_2$ triplet ground state was explored using a magneto optical trap combined with two-color photoassociation spectroscopy. Our spectroscopy also makes use of a two-photon transition, but starts from cold Feshbach molecules rather than from free atoms. Recent investigations of the $a^3\Sigma^+_u$ potential of $\text{Rb}_2$ in-

![FIG. 1: Dark-state spectroscopy scheme for the $^{87}\text{Rb}_2$ $a^3\Sigma^+_u$ potential. Lasers 1 and 2 couple the molecular levels $|j\rangle$ and $|\nu\rangle$ to the excited level $|e\rangle$ with Rabi frequencies $\Omega_1, 2$, respectively. Laser 1 is kept on resonance while laser 2 can be tuned to any level of the $a^3\Sigma^+_u$ potential. Inset: Bound state level of Feshbach molecules as a function of magnetic field $B_z$. The dashed line gives the position of the Feshbach resonance. The dot marks the Feshbach molecule state used in the experiments.]
clude the work of [10, 17] and [18]. Using one-color photoassociation of the $3\Sigma_u^+$ potential of laser cooled $^{85}$Rb, reference [10] put tight constraints on the position of the repulsive wall of the $3\Sigma_u^+$ potential but was not able to resolve the vibrational structure. The two other groups determined several ro-vibrational levels using fluorescence spectroscopy [17] or pump-probe photoionization spectroscopy of Rb$_2$ formed on helium nanodroplets [18]. Our work goes well beyond these measurements as we fully resolve hyperfine, rotational and Zeeman structure for almost all vibrational states. Highly precise data of the asymptotic behavior of the coupled $3\Sigma_u^+-\Sigma_u^+$-system is contained in the large set of observed Feshbach resonances [19–22] and in the two-photon photoassociation measurements of four weakly bound levels at zero magnetic field by [23].

This article is organized as follows: Section II presents the experimental setup and typical dark state spectroscopy scans. Section III discusses the relevant quantum numbers of our studies and the assignment of the observed lines. Section IV is a short summary of the coupled-channel model and the optimization procedure of the Born-Oppenheimer potentials. Section V discusses the progression of the substructure of the vibrational manifolds. We conclude the paper with a summary and an outlook towards further experiments in section VI.

II. EXPERIMENTAL SETUP AND DARK STATE SPECTROSCOPY

The starting point for our experiments is a 50$\mu$m-size pure ensemble of $3\times 10^4$ weakly bound Feshbach molecules which have been produced from an atomic Bose-Einstein condensate of $^{87}$Rb by ramping over a Feshbach resonance at a magnetic field of 1007.4 G (1 G = $10^{-4}$ T) [24]. They are trapped in the lowest Bloch band of a cubic 3D optical lattice with no more than a single molecule per lattice site [25]. 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 prevent the molecules from colliding with each other, which suppresses collisional decay. We observe lifetimes of a few hundred ms. After producing the Feshbach molecules, the magnetic field is set to 1005.8 G where the spectroscopy is carried out. At this magnetic field, the binding energy of the Feshbach molecules is 4.4(3) MHz×h (Fig. 1 inset).

Our dark state spectroscopy works as follows: The Feshbach molecules in state $|i\rangle$ are irradiated by simultaneous rectangular pulses from lasers 1 and 2. The pulses typically last 10 $\mu$s with Rabi frequencies $\Omega_1$ and $\Omega_2$, respectively (Fig. 1). We keep laser 1 resonant with the $|i\rangle - |e\rangle$ transition and at a power $I_1$ of about 0.1 mW ($\Omega_1 = 2\pi \times 0.3$ MHz) such that in the absence of laser 2 about half of the molecules are lost by spontaneous emission from $|e\rangle$. Laser 2 with its power $I_2$ (up to a few hundred mW) is scanned. As long as laser 2 does not hit an $|e\rangle - |v\rangle$ resonance, laser 1 will continue to induce losses. However, when an $|e\rangle - |v\rangle$ resonance occurs, the initial state $|i\rangle$ is projected onto a dark state $|\Psi_{dark}\rangle = (\Omega_2|i\rangle - \Omega_1|v\rangle)/\sqrt{\Omega_1^2 + \Omega_2^2}$. Molecules in this dark state are shielded from excitation to the short-lived level $|e\rangle$ [26]. This leads to a suppression of molecular losses. After the lasers are switched off we measure the number of molecules via a reverse magnetic field sweep through the Feshbach resonance, dissociating the remaining molecules in $|i\rangle$ into atoms which are detected by absorption imaging. These measurements are destructive, and for each point in a scan, a fresh sample of Feshbach molecules has to be prepared.

The level $|e\rangle$ has an excitation energy of about 295 THz×h with respect to $|i\rangle$ and a width $\Gamma = 2\pi \times 8$ MHz. Laser 1, a grating-stabilized diode laser, is Pound-Drever-Hall locked to a cavity which is in turn locked to an atomic $^{87}$Rb-line. Laser 2, a Ti:Sapphire laser, is free-running and typically drifts over a frequency range of a few MHz within seconds. Both lasers have a short-term laser line width of several tens of kHz. Their beams have a $1/e^2$ intensity waist radius of 130 $\mu$m at the molecular sample, through which they propagate nearly collinearly. They are polarized parallel to the magnetic bias field $B_z$ (pointing in the vertical direction) and thus can only induce $\pi$ transitions. The frequencies of both lasers are automatically read out using a commercial wavemeter (WS7 from HighFinesse). The binding energy $E_B$ of $|v\rangle$ minus the binding energy of our initial Feshbach state (4.4 MHz×h) corresponds to the frequency difference of the two lasers. The wavemeter has a nominal accuracy.

FIG. 2: (a) Binding energies $E_B(v)$ for the state $3\Sigma_u^+$, where $v$ is the vibrational quantum number. The line is the result of a coupled-channel model calculation after optimization of the Born-Oppenheimer potential. Five levels were not measured. (b) Residues i.e. difference between experimental data and theory. Large error bars belong to early measurements without simultaneous wavemeter readings of both lasers.
of 60 MHz after calibration. Over the course of days we have observed drifts of ±200 MHz, e.g. by repeatedly addressing the same spectroscopic line. Over the length of a few experimental cycles (5 minutes) the wavemeter is stable to within 10 MHz, which represents a random noise floor. Assuming a sufficiently smooth behavior of the wavemeter, drifts of the wavemeter typically affect the frequency measurements of laser 1 and laser 2 in a similar way, especially since the laser frequencies only differ by 3%. Thus, such common mode drifts cancel out in the binding energy to first approximation. Indeed, based on our experience with the wavemeter where we have measured binding energies of a few sharp lines over an extended period of time and via various intermediate levels we estimate the accuracy to reach 30 MHz. This includes peak position uncertainties due to variations of the number of molecules produced, as well as a frequency drift of laser 2 during the time between the laser pulse and wavelength measurement.

Fig. 2 a) shows the measured binding energies of the triplet potential as a function of the vibrational quantum number \( v \) at a magnetic field of 1005.8 G. There are 41 vibrational states with binding energies ranging from 5 MHz x \( h \) to about 7038 GHz x \( h \). The vibrational splitting between the two lowest vibrational levels, \( v = 0 \) and \( v = 1 \), is about 393 GHz. Each vibrational state has hyperfine, rotational, and Zeeman substructure. This structure is spread out over a range of about 20 GHz as shown in Fig. 3 for the states \( v = 0 \) and 6. These spectra typically consist of roughly 1000 points corresponding to an average step size of 20 MHz. Each point represents one production and measurement cycle which takes 28 s.

In each spectrum of Fig. 3 we observe some 10 lines which vary markedly in line width. The width of each line is determined by the coupling between the levels \( \ket{e} \) and \( \ket{v} \), i.e. the Rabi frequency \( \Omega_2 \). Interestingly, for our measuring scheme this width scales as \( \Omega_2^2 \) \( [27] \) and not as \( \Omega_2 \) \( [28, 29] \), as one might expect. We have taken advantage of this enhanced broadening when searching for lines and vibrational manifolds, which otherwise can be like looking for a needle in a haystack. For example, for \( v = 0 \) and an intensity \( I_2 \) of a few hundred mW we reached line widths of several GHz. The substructure of the desired vibrational level then appears essentially as a single broad line with a width of about 20 GHz. Once this level was found the power was reduced, in order to resolve its substructure.

In general, we expect spectra of different vibrational levels to be very similar. Up to \( v = 35 \) this is indeed the case. For \( v \geq 35 \) the vibrational manifolds start to overlap, as the splitting between them becomes smaller than 20 GHz. Spectra a) (\( v = 0 \)) and b) (\( v = 6 \)) of Fig. 3 are clearly similar. Some visible differences are artifacts, e.g. it seems that in spectrum b) two narrow lines are missing at \( E_B / h \approx 7021 \) GHz. This can be explained by the fact that the lines were narrower (width \( \leq 10 \) MHz) than the local step size of that scan and thus escaped observation.

![Fig. 3: Scans of two vibrational levels: a) \( v = 6 \), b) \( v = 0 \). Plotted is the remaining molecular fraction as a function of the binding energy \( E_B \), which basically corresponds to the laser difference frequency. The scans were recorded using an excited state \( \ket{e} \) with 1\( _K \) character. The labels s and d indicate rotational states \( N = 0 \) and 2, respectively. The numbers after the labels s or d indicate the position in the spectrum.](image)

### III. QUANTUM NUMBERS AND ASSIGNMENT

#### A. Quantum numbers

For a deeper understanding of the structure of the spectrum and its assignment we now discuss the relevant quantum numbers and selection rules.

For the weakly bound levels like the Feshbach state or the vibrational levels close to the atomic asymptote Hund’s coupling case \( (c) \) with atomic quantum numbers is most appropriate. Here none of the angular momenta couple to the molecular axis. The state vector is described by

\[
|f_\text{A}, f_\text{B}\rangle f, l, F, M\rangle,
\]

where \( f_\text{A}, f_\text{B} \) are the total angular momenta for atoms A and B, \( f \) is the sum of both atomic angular momenta, \( l \) is the mechanical rotation of the atomic pair, \( F \) is the total angular momentum of the pair and \( M \) is its projection onto a space fixed axis. At low magnetic fields the prepared Feshbach state \( |i\rangle \) can be approximated by the state vector \( |f_\text{A} = 2, f_\text{B} = 2, f = 2, l = 0, F = 2, M = 2 \rangle \).

At the magnetic field used in the experiment (1005.8 G), \( F \) is no longer a good quantum number because of only weak coupling between \( l \) and \( f \). A more appropriate state vector is

\[
|f_\text{A}, f_\text{B}\rangle f, m_f, l, m_l, M\rangle.
\]

\( M \) is a good quantum number, while for example, \( f_\text{A} \) and \( f_\text{B} \) have expectation values \( [30] \) of about 1.79 instead of quantum numbers \( f_\text{A} = f_\text{B} = 2 \) for 0 G.

Due to the strong hyperfine coupling of Rb and the large exchange energy, deeply bound levels of the triplet state can be described by Hund’s coupling case \( (b_\beta) \) at
molecules with even (odd) nuclear spin, \(I\) have either a total nuclear spin 
\[N\]

\[I\]

quantum numbers, \(I\) electron orbital angular momentum, and \(F\) and \(M\) have exactly the same meaning as in Hund’s case (e). The index \(\beta\) indicates that the nuclear spin \(I\) is not coupled to the molecular axis. Since both atoms are in the 5\(S\) configuration of Rb, the molecular electronic orbital angular momentum is zero. This means that \(N = I\) and that \(f\) is the same as in Hund’s case (e). Here we get

\[\left| N, m_N, (I, S)f, m_f, M\right\rangle,\]

as an appropriate state vector for higher magnetic fields, where \(M = m_N + m_f\). One can show that owing to the antisymmetry of the molecular wave function with respect to nuclear exchange (nuclear spin of \(^{87}\text{Rb} i = \frac{3}{2}\)), molecules with even (odd) \(N\) in the \(a^{3}\Sigma_{u}^{+}\) state must have either a total nuclear spin \(I = 1\) or \(3\) (\(J = 0\) or \(2\)) \[31, 32\]. For the \(X^{1}\Sigma_{g}^{0}\) singlet ground state this relation is reversed because it has \(g\) symmetry in contrast to the \(u\) symmetry of the triplet state. For large magnetic fields, \(f\) loses its meaning as \(S\) and \(I\) start to decouple.

Expectation values for the total nuclear spin and the electron spin for our Feshbach level are \(I = 1.56\) and \(S = 0.76\), respectively. Thus we have significant electronic singlet-triplet mixing and consequently also mixing of the basis vectors with different \(I\). In contrast, the excited intermediate state \(\left|e\right\rangle\) has well defined quantum numbers \(S\) and \(I\). Thus \(\left|e\right\rangle\) largely determines which quantum numbers the deeply bound \(a^{3}\Sigma_{u}^{+}\) levels will have in the Raman transition.

The intermediate level \(\left|e\right\rangle\) is located in the \(v' = 13\) manifold of the \(1^{3}\Sigma_{g}^{+}(5S_{1/2} + 5P_{3/2})\) potential. Due to significant effective spin-spin interaction, the vibrational manifold is split into two components, \(1_{g}\) and \(0_{g}\), separated by 47 GHz. As intermediate level \(\left|e\right\rangle\) we either choose a level with \(1_{g}\) character or with \(0_{g}\) character. Its rotational energy must be low because the Feshbach level has the lowest rotational quantum number \(N = 0\). As rotation is low in \(\left|e\right\rangle\), decoupling of \(S\) and \(I\) from the molecular axis by rotation is not yet important. We can then approximate the state \(\left|e\right\rangle\) by quantum numbers for Hund’s case \((a)\) where the index \(\alpha\) indicates that the nuclear spin \(I\) is coupled to the molecular axis,

\[\left|\Sigma, I\Omega_{I}, F, M\right\rangle.\]

The projections of the electronic and nuclear spin onto the molecular axis appear as quantum numbers \(\Sigma\) and \(\Omega_{I}\), respectively.

The \(\left|e\right\rangle\) level with \(1_{g}\) character is energetically the lowest within the \(1_{g}\) manifold. It has the quantum numbers \(S = 1, |\Sigma| = 1, I = 3, |\Omega_{I}| \approx 3, F \approx 2\) and \(M = 2\) for low magnetic fields \(B_{z}\). Its excitation energy is 294.6736(2) THz with respect to \(\left|i\right\rangle\) at a field of 1005.8 GHz.

The \(\left|e\right\rangle\) level with \(0_{g}\) character has an excitation energy of 294.6736(2) THz. It can be described by the quantum numbers \(S = 1, |\Sigma| = 0, I = 3, M = 2\) and \(F = 3\) at \(B_{z} = 0\). Because of its low hyperfine coupling the better choice of basis vector here is

\[\left|S\Sigma, (J)F, M\right\rangle,\]

where \(J\) results from the coupling of the electronic spin and the molecular rotation \((J = N + S)\). For our \(0_{g}\) \(\left|e\right\rangle\) level \(J\) is approximately zero. Our \(1_{g}\) \(\left|e\right\rangle\) state is a superposition of \(N = 1\) and 3.

As stated before, due to the laser polarization along the magnetic field only \(\pi\) transitions are allowed, which results in the selection rule \(\Delta M = 0\). Further, in a one-photon transition parity has to change. The Feshbach state \(\left|i\right\rangle\) has a total parity “plus” because it is a \(\Sigma_{g}^{+}\) state and \((-1)^{N} = 1\). Thus we can only address \(\left|e\right\rangle\) levels with “minus” parity and \(\left|e\right\rangle\) levels with “plus” parity. This means that the \(\left|e\right\rangle\) level must have an even rotational quantum number \(N = 0, 2, 4, ...,\) For the \(\left|e\right\rangle\) level only quantum numbers \(N = 1, 3, ...\) or superpositions of these are available. In fact, as the \(1^{3}\Sigma_{g}^{+}\) state is well described in a Hund’s case (a) basis, \(N\) is in general not a good quantum number for the \(\left|e\right\rangle\) level. The selection rule \(\Delta N = \pm 1\) for \(N\) determines the range of reachable levels for \(\left|e\right\rangle\) according to the superposition in \(\left|e\right\rangle\). The selection rules \(\Delta J = 0\) and \(\Delta S = 0\) are important for the transition \(\left|i\right\rangle\) to \(\left|e\right\rangle\). For the transition \(\left|i\right\rangle\) to \(\left|e\right\rangle\) they are, however, nearly irrelevant since \(I\) and \(S\) are not good quantum numbers for level \(\left|i\right\rangle\).

B. Assignment of spectral lines

Figure 4 shows measured and calculated (based on the coupled-channel model, see section IV) lines of the \(v = 6\) spectrum, where the excited state \(\left|e\right\rangle\) with \(0_{g}\) character was selected. The lines form three groups with the quantum numbers \(f = 4, 3, \) and \(2\), according to the hyperfine coupling of \(S = 1\) and \(I = 3\). This is a clear indication that the hyperfine energy is still dominant compared to the Zeeman energy.

Each group consists of one line with \(N = 0\) corresponding to a non-rotating molecule, and several lines with \(N = 2\) which are shifted to lower binding energy by about 2 GHz\(xh\) due to rotation. The fact that we do not observe lines with \(N > 2\) can be explained as follows: The excited state \(\left|e\right\rangle\) has “minus” total parity. Since \(J = 0\) and \(S = 1\), \(N\) must be equal to one and is also a good quantum number for this lowest level in the \(0_{g}\) manifold. Thus when using the state with \(0_{g}\) character only final states \(\left|e\right\rangle\) with \(N = 0, 2\) can be addressed in the \(a^{3}\Sigma_{u}^{+}\) state due to the selection rule \(\Delta N = \pm 1\).

The overall structure of each vibrational level can be understood with a relatively simple effective Hamiltonian \[33\]:

\[H = \frac{A}{2} S \cdot I + B_{e} N^{2} + \mu_{B} g_{S} S_{z} B_{z}\]
with the atomic hyperfine structure constant $A = 3.42 \text{ GHz} \times 4\pi^2/\hbar$, the total electronic and nuclear spin operator $\mathbf{S}$ and $\mathbf{I}$, respectively, and the operator for molecular rotation $\mathbf{N}$. $B_v$ is the rotational constant of the desired vibrational level $v$. The last term describes the Zeeman effect of the electronic spin when exposed to an external magnetic field $B_z$ in $z$-direction. The nuclear Zeeman term is neglected. The Zeeman effect can be evaluated for the case of strong hyperfine coupling such that $f$ (with $f = S + I$) is still a good quantum number. Using a simple vector model for $f$ one can derive a Landé factor $g_f$:

$$H = \frac{A}{2}\mathbf{S} \cdot \mathbf{I} + B_v \mathbf{N}^2 + \mu_B g_f m_f B_z$$

with $g_f = g_S/2 \left( 1 + S(S+1) - I(I+1) \right) / f(f+1)$ (1)

For each $f$, the $N = 2$ group is shifted to lower binding energy by $6B_v$ compared to $N = 0$, corresponding to about 2 GHz for the $v = 6$ manifold (see Figure 4). Each $N = 2$ group is split by the Zeeman energy according to the $m_f$ quantum number of each line. Only those lines which have quantum numbers where $M = 2 = m_f + m_N$ can be observed. The level $f = 3$ has a small $g_f$ factor (1/6 for $I = 3$), which gives rise to a small Zeeman splitting. Additionally, one sees that the splitting between $f = 4$ and $f = 2$, which would be about 12 GHz for the pure hyperfine part, is enlarged by a Zeeman contribution because of the different signs of $g_f$ for $f = 3$ and $f = 2$. In Figure 4 the expectation values for $m_f$ resulting from the coupled channel model are given in the upper row and show that these lead to good quantum numbers for $f = 4$ and $f = 2$ but are less good for $f = 3$, where the hyperfine and electronic Zeeman energies are small. The mixing of states with different $m_f$ for $f = 3$ is not included in the simple model of Eq. (1).

As discussed before, for the intermediate state with $0^+_g$ character we exclusively observed $N = 0$ and $N = 2$ levels in the $a^3\Sigma_u^+$ potential. This restriction does not necessarily apply when using the intermediate level $|e\rangle$ with $1^+_g$ character. The corresponding spectrum in Figure 3(a) shows the same $v = 6$ manifold as in Figure 4 only $|e\rangle$ has $1^+_g$ instead of $0^+_g$ character. It has additional lines (at $\sim$4838 GHz and at $\sim$4832 GHz) which match the predicted positions of $N = 4$ levels.

As mentioned in Section III.A the level $|e\rangle$ with $1^+_g$ character would be described by a superposition of $N = 1$ and $N = 3$ states in a Hund’s case (b) basis. We thus expect to see transitions to levels with $N = 0, 2, 4$ of the $a^3\Sigma_u^+$ state according to the selection rule $\Delta N = \pm 1$. In order to avoid confusion, we note that the $N = 0$ and $N = 2$ lines between 4825 GHz and 4830 GHz which are clearly visible in Figure 4 are weak or are not even observed in Figure 4. For the same reasons as discussed at the end of section III the experimental step size of about 10 MHz might have been too large compared to the narrow line widths for these transitions to be seen.

It was not always necessary to carry out a complete scan as in Figure 4 in order to assign quantum numbers to observed lines in arbitrary vibrational levels. Often it was sufficient to measure a few characteristic lines and splittings and to compare them to the calculated spectrum. These data were then used to optimize the coupled channel model along with its $a^3\Sigma_u^+$ and $X^1\Sigma_g^+$ Born-Oppenheimer potentials.

**IV. COUPLED-CHANNEL MODEL AND OPTIMIZATION OF THE $a^3\Sigma_u^+$ POTENTIAL**

In our work we use a coupled-channel model [35–37] that can calculate all bound states of the $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$ states, which correlate with the atomic asymptote $5^2S_{1/2} \oplus 5^2S_{1/2}$. The program has helped us with the search for lines as well as with their identification. Using our data we are able to optimize the Born-Oppenheimer potential of the $a^3\Sigma_u^+$ state as well as to improve the potential of the ground state $X^1\Sigma_g^+$ given in [39]. In the following we briefly describe the model and explain how the $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$ Born-Oppenheimer potentials are optimized.

To cover the full range of experimental data by a single theoretical model, only a coupled channel analysis is adequate. It includes the calculation of the molecular bound states as well as the scattering resonances. It takes into account the $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$ potential functions, the hyperfine coupling, the Zeeman interaction, rotation and the effective spin–spin interaction. Such a theoretical approach is described in several papers, e.g. [38].

For the present analysis we include our measurements covering 135 lines of the $a^3\Sigma_u^+$ state as well as data from
other work. For the $X^1\Sigma_g^+$ ground state we added data from Fourier transform spectroscopy by Seto et al. \cite{39} with more than 12000 lines. We also include measurements of Feshbach resonances for the three isotopologues $^{85}\text{Rb}_2$, $^{87}\text{Rb}_2$, and $^{85}\text{Rb}^{87}\text{Rb}$ \cite{19,22}, the four asymptotic levels from \cite{23}, and measurements from Fourier transform spectroscopy for the $a^3\Sigma_u^+$ state reported by Beser et al. \cite{17}.

The full Hamiltonian (cf. \cite{38,40,41}) for a pair of atoms $A$ and $B$ can be written in the form

$$H = T_n + U_X(R)P_X + U_a(R)(1 - P_X) + a_A(R)\vec{s}_A \cdot \vec{i}_A + a_B(R)\vec{s}_B \cdot \vec{i}_B + \left[(g_u A^z A - g_i A^z i_A) + (g_u B^z B - g_i B^z i_B)\right] \mu_B B_z + \frac{2}{3}\alpha(R)(3S_z^2 - S^2).$$

(2)

In the present case of the homonuclear molecule $^{87}\text{Rb}_2$ the parameters with index $A$ are equal to those of index B. The first term in the first line shows the kinetic energy $T_n$ where we take the atomic masses from recent tables by G. Audi et al. \cite{12}. The next two terms describe the potential energies $U_X$ and $U_a$ for the motion of the atoms, where $P_X$ and $1 - P_X$ are projection operators on to the uncoupled states $X$ and $a$, respectively. $R$ corresponds to the internuclear separation of the two atoms. The second line shows the hyperfine interaction between the atomic electron spins $\vec{s}_A,B$ and the atomic nuclear spins $\vec{i}_A,B$. The main contribution to the functions $a_{A,B}(R)$ is the Fermi contact term. The $R$ dependence of the hyperfine parameters accounts for several effects: It takes into account the electronic distortions of one atom by the other, i.e. the binding, and an effective coupling of the electron spin of one atom with the nuclear spin of the other atom.

We start with $R$-independent atomic coupling constants taken from a compilation by Arimondo et al. \cite{43}. These constants are later refined by a simple Ansatz for the $R$ dependence (discussed later in Eq. (8)). We neglect the nuclear quadrupole moment in the hyperfine interaction, which might come into play for deeply bound levels. The third line in Eq. (2) gives the Zeeman energy from the coupling of the electron spin and the nuclear spin with an external homogeneous magnetic field $B_z$ in $z$ direction. The electronic and nuclear $g$-factors for the atomic ground state of the Rb isotopes are taken from the report in \cite{43}. This term couples states with different $f$ quantum numbers. The last line contains the spin-spin interaction which couples different $N$ states of basis (b). It is formed by the total molecular spin $S$ and its projection on the molecule fixed axis $Z$. The parameter $\lambda$ is a function of $R$, of which one part has $1/R^3$ dependence as a result from the magnetic dipole-dipole interaction. In addition, $\lambda$ contains contributions from second order spin-orbit interactions. The final analysis showed that such a contribution is significant within the achieved experimental accuracy. For example, this was important for the precise location of Feshbach resonances involving $l = 1$ and $l = 2$ bound levels.

The functional form of the two Born-Oppenheimer potentials, $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$, is split into three regions on the internuclear separation axis $R$: the short range repulsive wall ($R < R_{SR}$), the asymptotic long range region ($R > R_{LR}$), and the intermediate deeply bound region in between. The analytic form of the potentials in the intermediate range, $U_{IR}$, is described by a finite power expansion of a nonlinear function $\xi$ which depends on the internuclear separation $R$,

$$U_{IR}(R) = \sum_{i=0}^{n} a_i \xi^i(R),$$

(3)

$$\xi(R) = \frac{R - R_m}{R + b R_m}.$$  

(4)

Here the $a_i$ are fitting parameters (see table II). We choose $b$ and $R_m$ such that only few parameters $a_i$ are needed for describing the steep slope at the short internuclear separation side and the much smaller slope at the large $R$ side. $R_m$ is chosen close to the value of the equilibrium separation. The potential is extrapolated for $R < R_{SR}$ by the short range part $U_{SR}$ with:

$$U_{SR}(R) = u_1 + u_2/R^{N_x}.$$  

(5)

We adjust the parameters $u_1$ and $u_2$ to get a continuous transition at $R_{SR}$. The final fit uses $N_x \approx 4.5$ for both the $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$ states.

For large internuclear distances ($R > R_{LR}$) we adopted the standard long range form of molecular potentials

$$U_{LR}(R) = -C_6/R^6 - C_8/R^8 - C_{10}/R^{10} \pm E_{exch},$$

(6)

where the exchange contribution given by \cite{44}

$$E_{exch} = A_{ex} R^7 \exp(-\beta R)$$

(7)

is negative for the singlet and positive for the triplet potential. By adjusting the parameter $a_0$ in Eq. (8) we can assure a continuous transition from $U_{IR}$ to $U_{LR}$. As mentioned, the data on hand include three different isotopologues, namely $^{85}\text{Rb}_2$, $^{87}\text{Rb}_2$, and $^{85}\text{Rb}^{87}\text{Rb}$. Using a model developed earlier for LiK \cite{15} we checked in the final calculations that the data are not sufficiently precise to extract deviations from the Born-Oppenheimer approximation. Thus we derive the potentials without any mass scaling correction.

Having discussed the complete physical model, we are now ready to calculate all the relevant bound state energies and scattering properties to compare them with the experimental data. We have decided to evaluate the Hamiltonian in Hund’s basis (e) as $f$ is still a relatively good quantum number. This is due to the fact, that the hyperfine interaction is larger than the Zeeman interaction in our experiment. As the total electron spin is not a good quantum number in Hund’s case (e), the choice of this basis leads to significant non-diagonal matrix elements from the Born-Oppenheimer potentials, which are given for a pure singlet or triplet state.
We evaluate the free parameters of a model with a self-consistent iteration loop and alternate between: (i) coupled channel calculations of the full Hamiltonian and (ii) solving the Schrödinger equation separately for the states $X^1\Sigma^+_g$ and $a^3\Sigma^+_u$ using only the first line of Eq. 2 and applying the Numerov procedure. The coupled channel calculations in step (i) are used to determine the hyperfine and Zeeman structure. From this we construct hyperfine free spectroscopic data. This data is the input for the Born-Oppenheimer potential fits in step (ii). We incorporate the fitting routine for the plain Born-Oppenheimer potentials in step (ii). The optimization of the singlet and triplet potentials is done simultaneously as both potentials have a common asymptote. These asymptotic potentials are given in Eq. 6 with equal dispersion coefficients.

Normally, the iteration loop between the potential function fit and the coupled channel calculation for producing hyperfine structure free data converges in a few steps, but we observed some systematic deviations between measurements and calculations. Specifically the hyperfine splitting showed variations of a few percent within the vibrational ladder. Even though our experimental accuracy is not better than $30 \text{ MHz}$ such small variations are observable since the hyperfine splitting in $^{87}\text{Rb}$ of $12 \text{ GHz}$ is so large.

In order to theoretically account for the hyperfine variations we extended the model. We changed the fixed atomic hyperfine constant to another value for a deeply bound dimer, $a_{\text{A/B}} = a_{\text{Rb}} \left(1 + \frac{c_f}{e^{(R-R_0)/\Delta R}} + 1\right).$ (8)

Here $a_{\text{Rb}}$ is the atomic hyperfine constant, $c_f$ the fractional change of the constant and $R_0$ and $\Delta R$ describe the switching distance and its width, respectively. We also tried several other simple switching functions, which produced for equal fit quality. The function in Eq. 8 is easily applicable for other isotopes by introducing the proper atomic hyperfine constant, because the scaling $c_f$ will be independent of the isotope. We chose $R_0 = 11.0 \ a_0$ and $\Delta R = 0.5 \ a_0$ (where $a_0 = 0.5292 \times 10^{-10} \text{ m}$ is the Bohr radius), such that switching takes place approximately at the minimum of the $a^3\Sigma^+_u$ potential. From our fits we obtained an amplitude $c_f = -0.0778$, which corresponds to a variation of the hyperfine coupling across the potential depth of up to 8%. The influence of this hyperfine variation within an individual vibrational manifold will be smaller because of the averaging of Eq. 8 over the vibrational wave function. As mentioned before, also the spin-spin interaction needs optimization in order to explain systematic shifts of Feshbach resonances in s-wave and p-wave scattering channels, as measured in 10. The spin-spin interaction couples different partial waves $l$ subject to the selection rule $\Delta l = 0, \pm 2$ such that resonances in a s-wave scattering channel involve bound states with $l = 0$ and $l = 2$. The spin-spin interaction splits the resonances according to $|m_l|$, the projection quantum number of rotation on the space fixed axis. We use a simple functional form for $\lambda(R)$ in Eq. 2

$$\lambda(R) = -\frac{3}{4}a^2 \left(\frac{1}{R^3} + a_{\text{SO}} \exp(-b(R-R_{\text{SO}}))\right),$$

that consists of two terms. The first term represents the magnetic dipole-dipole interaction and the second term is the second order spin-orbit contribution. If Eq. 9 is given in atomic units, $a$ is the fine structure constant. Since the few data at hand cannot be highly sensitive to the actual function, we adopted values for $b$ and $R_{\text{SO}}$ from a theoretical approach by Mies et al. for $\text{Rb}_2$ [14] ($b = 0.7196 \ a_0^{-1}$ and $R_{\text{SO}} = 7.5 \ a_0$). We fitted the parameter $a_{\text{SO}}$, which yielded $a_{\text{SO}} = -0.0416 \ a_0^{-3}$. With these parameters the second part in Eq. 9 contributes significantly to the effective spin-spin interaction in the internuclear separation interval $R < 20a_0$. This affects bound levels of the triplet states that determine the Feshbach resonances. After optimization we achieve an accuracy of 0.1G for the position of the Feshbach resonance. This correction to the constant $\lambda$ does not influence the description of the other bound states within their uncertainty.

Finally, we found that we can improve the fit by adding to the long range formula Eq. 6 a term of the form $-C_{26}/R^{26}$, and retaining all constraints such as continuity as before. From our fits we obtain an amplitude $C_{26}$ which contributes about a thousandth of the total long range energy at the connection point $R_{\text{LR}}$. The exponent of 26 was chosen so that the term is negligible outside a small region around the long range connection point $R = R_{\text{LR}}$.

The final parameter sets of the potentials are shown in table I and II for the singlet and triplet states, respectively. The derived potentials and the corrections defined above agree very closely with all observations to within their experimental uncertainties, and the normalized standard deviation (i.e. standard deviation / experimental uncertainty) is close to one. In fact, depending on which of our experimental data sets (hyperfine free spectra, binding energies from dark state spectroscopy or Feshbach resonances) we compare to the model calculations, the normalized standard deviations only vary slightly, ranging from 1.01 to 1.3. The normalized standard deviation from the joint calculation over the huge body of ro-vibrational energies (12459 data points from the states $X^1\Sigma^+_g$ and $a^3\Sigma^+_u$) is about 1.01, which is quite satisfactory.

As another result of our analysis we were able to eliminate an ambiguity in the rotational assignment of the Fourier transform spectroscopy data reported by Beser et al. for the state $a^3\Sigma^+_u$ [17]. The authors stated in the rotational assignment an ambiguity by $\Delta N = \pm 1$. We determined that the shift of the rotational quantum number must be $\Delta N = +1$. Afterwards we used the data from [17] with that assignment for the further fits. The result in Table III includes these data and will give a bet-
ter confidence in predicting rotational levels with higher rotational quantum numbers.

V. PROGRESSION OF VIBRATIONAL LEVELS AND THEIR SUBSTRUCTURE

In the following we will discuss interesting insights which we have gained from our analysis of the coupled system. In particular we investigate the progression of several quantities in the vibrational ladder and the mixing of singlet and triplet states. We concentrate on the details of the $a^3\Sigma_u^+$ state, because it was studied in full resolution of hyperfine and Zeeman energy over the whole vibrational ladder for the first time. Such a body of data does not exist for any other alkali dimer.

A. Vibrational ladder and rotational progression

We return to the vibrational states shown in Fig. 2 which allows us to compare in detail the optimized coupled-channel model with our experimental findings for all vibrational states.

![Energy splitting](image)

FIG. 5: Energy splitting $\Delta E_B$ between the "s1"-level ($N = 0$) and the "d1"-level ($N = 2$) for a given vibrational quantum number $v$. Large error bars correspond to early measurements without simultaneous wavemeter readings (see text). The continuous line is a calculation based on the coupled channel model.

The binding energies given in Fig. 2a) correspond to the most deeply bound level in each vibrational level, i.e. the state with quantum numbers $N = 0$, $f = 2$ (at 0 G) and $M = 2$. We will refer to this level as "s1". The "s1" level of $v = 0$ in the $a^3\Sigma_u^+$ potential is also the lowest bound state in that potential and has an observed binding energy of $(7038.067 \pm 0.050) \text{GHz} \times \hbar$ at 1005.8 G with respect to the lowest atomic asymptote $f_A = 1, m_A = 1$ and $f_B \approx 1, m_B = 1$. A list of all the other measured and calculated bound state energies together with their expectation values of the quantum numbers can be found in the supplementary material [47].

FIG. 2b) shows the residues between our experimental "s1" data and the optimized model. In general the model

| $R < R_{SR}$ | 3.126 Å |
|-------------|----------|
| $N$         | 4.5389   |
| $a_1^*$     | -0.638904880 $\times 10^4$ cm$^{-1}$ |
| $a_2^*$     | 0.112005361 $\times 10^7$ cm$^{-1} \cdot A^N$ |

| $R_{SR} < R \leq R_{LR}$ | 11.000 Å |
|----------------------------|---------|
| $b$                       | -0.14   |
| $R_{m}$                   | 4.209912760 Å |
| $a_0$                     | -3993.592873 cm$^{-1}$ |
| $a_1$                     | 0.00000000000000000 cm$^{-1}$ |
| $a_2$                     | 0.282009372927346137 $\times 10^5$ cm$^{-1}$ |
| $a_3$                     | 0.560425000209256905 $\times 10^4$ cm$^{-1}$ |
| $a_4$                     | -0.423962138510562945 $\times 10^4$ cm$^{-1}$ |
| $a_5$                     | -0.598558665058841584 $\times 10^5$ cm$^{-1}$ |
| $a_6$                     | -0.162613532034769596 $\times 10^5$ cm$^{-1}$ |
| $a_7$                     | -0.406142102246254944 $\times 10^{-6}$ cm$^{-1}$ |
| $a_8$                     | 0.19523741535279586 $\times 10^{-6}$ cm$^{-1}$ |
| $a_9$                     | 0.413823663033582582 $\times 10^{-6}$ cm$^{-1}$ |
| $a_{10}$                  | -0.45543248828921501 $\times 10^{-6}$ cm$^{-1}$ |
| $a_{11}$                  | 0.5466749015721098 $\times 10^{-6}$ cm$^{-1}$ |
| $a_{12}$                  | 0.663194778861331940 $\times 10^{-6}$ cm$^{-1}$ |
| $a_{13}$                  | -0.558341849704095051 $\times 10^{-8}$ cm$^{-1}$ |
| $a_{14}$                  | -0.573987344918535471 $\times 10^{-9}$ cm$^{-1}$ |
| $a_{15}$                  | 0.102010964189156187 $\times 10^{-10}$ cm$^{-1}$ |
| $a_{16}$                  | 0.3000410506311035 $\times 10^{-10}$ cm$^{-1}$ |
| $a_{17}$                  | -0.893187252759830856 $\times 10^{-10}$ cm$^{-1}$ |
| $a_{18}$                  | -0.736002541433475111 $\times 10^{-10}$ cm$^{-1}$ |
| $a_{19}$                  | 0.243130640980355225 $\times 10^{-11}$ cm$^{-1}$ |
| $a_{20}$                  | -0.786514776934984840 $\times 10^{-10}$ cm$^{-1}$ |
| $a_{21}$                  | -0.102470557344862152 $\times 10^{-12}$ cm$^{-1}$ |
| $a_{22}$                  | 0.895155811349267758 $\times 10^{-11}$ cm$^{-1}$ |
| $a_{23}$                  | 0.830355322356509201 $\times 10^{-11}$ cm$^{-1}$ |
| $a_{24}$                  | -0.150102297761234375 $\times 10^{-12}$ cm$^{-1}$ |
| $a_{25}$                  | 0.586778574293387071 $\times 10^{-11}$ cm$^{-1}$ |

TABLE I: Parameters of the analytic representation of the potential of state $X^1\Sigma_u^+$. The energy reference is the dissociation asymptote and the term energy $T_e^X$ is the depth of the potential. Parameters with * are set for continuous extrapolation of the potential and those with ** see text for interpretation.

| $R > R_{LR}$ | |
|--------------|---------|
| $C_0$        | 0.2270032 $\times 10^8$ cm$^{-1} \cdot A^6$ |
| $C_8$        | 0.7782886 $\times 10^6$ cm$^{-1} \cdot A^8$ |
| $C_{10}$     | 0.2868869 $\times 10^{11}$ cm$^{-1} \cdot A^{10}$ |
| $C_{26}^{**}$| 0.2819810 $\times 10^{26}$ cm$^{-1} \cdot A^{26}$ |
| $A_{ex}$     | 0.1317786 $\times 10^{-6}$ cm$^{-1} \cdot A^{-1} \cdot \gamma$ |
| $\gamma$     | 5.317689 |
| $\beta$      | 2.093816 Å$^{-1}$ |

Derived constants:

- Electrical distance: $R_e^X = 4.20991(5)$ Å
- Electronic term energy: $T_e^X = -3993.5928(30)$ cm$^{-1}$
agrees very well with the measurements to within the error bars. The data points with larger error bars belong to early measurements without simultaneous wavemeter reading of both lasers, which leads to a significant increase in the experimental uncertainty (see section [I]).

We now investigate the progression of the rotational splitting in the vibrational ladder. For this, we consider the “s1” level ($N = 0$) and its nearest neighbor in our spectra with ($N = 2$) which we call “d1” (see Figs. 3 and 4). The “s1” and “d1” levels both have $f = 2$ and $m_f = 2$. Thus the splitting between them is to a high degree rotational energy. The splitting decreases with increasing $v$, which is due to the fact, that the mean distance between the Rb$_2$ nuclei (and hence the effective moment of inertia) increases as $v$ increases. We have directly observed this behavior in our experiments (see Fig. 6). There is very good agreement between the experimental data and the calculation (continuous line) using the optimized potential of the $a^3\Sigma_u^+$ state.

![Fig. 6](image-url)
B. Hyperfine splitting and singlet-triplet mixing

It is instructive to investigate the progression of the multiplet structure of the vibrational levels. Figure 6(a) shows calculated levels for \( M = 2 \) stacked on top of each other for increasing \( v \) of the \( a^3\Sigma_u^+ \) potential. We concentrate on the triplet states \( (S = 1) \) with rotation \( N = 0, 2 \) and we restrict ourselves further to triplet levels with \( I = 3 \). Additionally, we show singlet levels \( (S = 0) \) with \( I = 2 \) that are located in the vicinity of the triplet levels. Thus, the typical stick spectrum of each vibrational manifold in the \( a^3\Sigma_u^+ \) state looks like the one in Fig. 4.

There are three groups of lines with \( f = 4, 3, 2 \), respectively. The vibrational quantum number \( v \) runs from 0 to 34, where the multiplets do not yet overlap for different vibrational levels.

In order to properly stack the data, we have chosen the level with \( N = 0 \), \( f \approx 3 \) to be the energy reference \( (\Delta E_B = 0) \) for each vibrational level. We call this level “s2” (see also Figs. 3 and 4). This level is quite insensitive to mixing with singlet levels which makes it a good reference because there is no singlet level with \( f = 3 \) and even parity for direct coupling. It is clear from Fig. 6(a), that the multiplet structure of different vibrational manifolds is similar, at least from \( v = 0 \) to about \( v = 30 \) as expected from the simple model Hamiltonian in Eq. 4.

The structure changes in a smooth and monotonical way with \( v \). For each of the quantum numbers \( f = 4, 3, 2 \) the splitting between \( N = 0 \) and \( N = 2 \) decreases with increasing \( v \) as discussed previously in section IV A.

Appreciable mixing of a singlet and a triplet level can occur when the two levels with \( f = 2 \) are located energetically closely enough, in our case within a few GHz, corresponding to the strength of the hyperfine interaction. One effect of mixing is a shift of the level positions due to level repulsion, clearly seen in Fig. 6(b). For \( v = 24 \), for example, the triplet lines of \( f = 2 \) are pushed to the left by about 0.4 GHz by the close singlet levels on the right hand side. For \( v < 20 \) we also observe narrow coincidences between triplet and singlet levels, e.g. for \( v = 15 \). Here almost no perturbation appears in the graph, in contrast to the case \( v = 24 \). We attribute this to a significantly lower overlap of the vibrational wavefunctions of the singlet and triplet levels for the case \( v = 15 \) compared to that of \( v = 24 \). For vibrational quantum numbers \( v > 30 \) mixing is very strong and happens for every vibrational level. Because the long range behaviour of the \( a^3\Sigma_u^+ \) and \( X^1\Sigma_g^+ \) states is similar, the overlap of the wave functions will become large for high \( v \). The vibrational spacing will become similar to the hyperfine splitting, and the state vectors here are best described by Hund’s coupling case (e) i.e. quantum numbers of atom pairs.

Singlet-triplet mixing not only occurs for triplet molecules with \( I = 3 \) but also for \( I = 1 \). Figure 6(b) shows \( (N = 0) \) triplet levels with \( I = 3 \) and \( I = 1 \) for \( v = 25 \) to 34. The repulsion of the \( I = 1 \) levels from the singlet levels is clearly visible. The figure shows an avoided-crossing-like behavior for the levels on the right as a function of \( v \), indicating the strong mixing between \( I = 3 \) and \( I = 2 \) which also means that \( u/g \) symmetry is broken for these levels. Further, our calculations show that only levels with the same \( f \) and \( N \) quantum numbers mix considerably. The singlet lines shown here have \( f = 2 \) and \( N = 0 \). Apparently, despite the relatively strong magnetic fields of about 1000 G \( f \) is still quite a good quantum number. Indeed, \( f \) appears as quantum number in both state vectors for Hund’s case (b) and (e) and loses its meaning only for much higher magnetic fields. \( N \) is good due to the small effective spin-spin interaction.

The shift in position due to mixing can be traced more clearly with a simple difference method discussed in the following. Fig. 7 shows the “discrete second derivative” of \( E_B(v) \), i.e. \( \delta^2E_B(v) = E_B(v + 1) - 2E_B(v) + E_B(v - 1) \). The solid curve connects the points from the “s1” levels while the diamonds correspond to the “s2”-state.

We have confirmed the singlet-triplet mixing experimentally. Fig. 8 shows scans of parts of the vibrational levels \( v = 28, 31, 33 \) where the intermediate level \( \langle e \rangle \) with \( 1_g \) character was used (see also Fig. 3). The “s2”-level is chosen to be the energy reference at \( \Delta E_B = 0 \) as before. For \( v = 28 \) we observe a line structure similar to that of Figs. 5 and 3. Thus we take the \( v = 28 \) spectrum as reference of the pure case ”triplet”. In fact, from our calculations we see that the next singlet level is located about 30 GHz away. This detuning gives rise to only a very small mixing which slightly lowers the triplet character of the “s1”-level to 0.99. The singlet level obtains a triplet character of 0.02. However, due to the selection rule \( \Delta S = 0 \), the transition to the intermediate state \( \langle e \rangle \) with its very pure triplet character would simply be too
weak to see.

This situation changes drastically for \( v = 31 \) and 33. Two additional lines are visible in the spectrum which originate from singlet states with \( M = 2, N = 0 \) and 2. Here the singlet-triplet mixing is close to 40% which makes the singlet lines easily detectable. Additionally, for \( v = 31 \) the “s1” and ”d1” components are shifted to lower values than expected from the reference spectrum \( v = 28 \) due to repulsion by the singlet component on the high energy side. In the case of \( v = 33 \) the singlet component pushes the “s1” and ”d1” in the opposite direction. Our calculations show that even the chosen energy reference “s2” starts to show mixing, indicated by its reduced triplet character of 0.98. In parallel to the singlet-triplet mixing, the quantum number \( I \) loses its meaning as well, e.g. the level “s1” of \( v = 33 \) has an expectation value for \( I \) of 2.75 instead of 3, due to a significant contribution of \( I = 2 \) from the singlet state. Comparing the stick spectrum line positions with observed lines in Fig. 8 we note the very nice agreement between experiment and theory. We want to mention that we measured the singlet levels at the predicted positions from first calculations. This emphasizes the predictive power of the presented model.

The fact that we observe singlet-triplet mixing for relatively deeply bound levels with binding energies of a few hundred GHz\( \times h \) is already quite interesting. In addition, it provides valuable information for fixing the energy position of the triplet levels with respect to the singlets with high precision. This is especially important for the large body of data of the singlet system, see section IV, which was obtained with no connection to the triplet state [39].

### C. Franck-Condon overlap

When scanning over all vibrational levels, the transition matrix elements for the transition from \( |e\rangle \) to \( |v\rangle \) are not constant but oscillate as a function of \( v \). This oscillation is mainly due to variations in the Franck-Condon overlap between the \(|e\rangle\), \(|v\rangle = 13\) vibrational wave function and the vibrational wave functions \(|v\rangle\) of the \( a^3\Sigma_u^+ \) potential. Figure 9 shows the normalized transition matrix element, \( c_2 = \Omega_2(v)/(2\pi\sqrt{I_2}) \), where \( \Omega_2 \) is the Rabi frequency and \( I_2 \) is the intensity of laser 2. \( \Omega_2 \) is determined from the measured width of the dark resonance [48, 49]. For these measurements we used the excited level \( 1_g \) as \( |e\rangle \) and the “s1” levels as \( |v\rangle \) of the \( a^3\Sigma_u^+ \) state. The transition matrix element \( c_2 \) varies from about (0.2 to 33) MHz/\( \sqrt{\text{Wcm}^{-2}} \). In terms of a dipole moment, \( \langle |e\rangle |v\rangle = \Omega_2(v)/(2\pi\times h\times e|c|/2 \), this corresponds to (0.05 to 8.0)\( \times 10^{-30} \) Cm.

In comparison, the amplitude for the transition between \( |i\rangle \) and \( |e\rangle \) is \( \Omega_1/\sqrt{I_1} \approx 0.4 \) MHz/\( \sqrt{\text{Wcm}^{-2}} \). We determine \( \Omega_1 \) from resonant excitation, measuring how quickly \( |i\rangle \) molecules are lost for a given laser intensity \( I_1 \). The data in Fig. 9 can be used to fix the position of the \( 1^3\Sigma_u^+ \) potential relative to the \( a^3\Sigma_u^+ \) potential applying the Franck-Condon approximation.

### VI. CONCLUSION AND OUTLOOK

In this paper we demonstrate high resolution dark state spectroscopy of ultracold \(^{87}\text{Rb}_2\) molecules. We are able to resolve the vibrational, rotational, hyperfine and Zee- man structure of the lowest \( a^3\Sigma_u^+ \) potential with an absolute accuracy as high as 30 MHz. We find that the hy-
TABLE III: Scattering lengths (in Bohr radius, $a_0 = 0.5292 \times 10^{-10}$ m). $a_{\text{lowest}}$ gives the scattering length of the energetically lowest hyperfine state at $B_z = 0$.  

| Isootope | $a_{\text{singlet}}$ | $a_{\text{triplet}}$ | $a_{\text{lowest}}$ | Rb + Rb $(f, m_f) + (f, m_f^\prime)$ |
|---------|----------------------|----------------------|----------------------|----------------------------------|
| 87/87   | 90.35                | 99.04                | 100.36              | (1, 1) + (1, 1) |
| 85/85   | 272.0                | -386.9               | -460.1              | (2, 2) + (2, 2) |
| 87/85   | 11.37                | 201.0                | 229.4               | (1, 1) + (2, 2) |

The potential we obtain a model that can quite accurately predict all vibrational levels in the $a^3\Sigma_u^+$ and $X^1\Sigma_g^+$ potentials for different ranges of rotational quantum numbers. After reassigning recent data from Fourier transform spectroscopy [17] we extend the range of applicability to rotational states as high as $N = 70$ for the $a^3\Sigma_u^+$ potential. Because of this reassignment also the molecular parameters like the equilibrium internuclear separation $R_e$ or the dissociation energy $D_e$ have changed significantly compared to values reported in [17]. The new values are given in Table III. For rotational levels with $N \leq 4$ the model calculations for triplet levels of any vibrational level should have a precision similar to that of our measurements, i.e. about 30 MHz. For higher $N$ this precision will increasingly degrade resulting from the reduced accuracy of the data from [17] of about 300 MHz for $N = 70$. Compared to [39] the potential of the ground state $X^1\Sigma_g^+$ is significantly improved close to the atomic asymptote by including data on the mixed singlet-triplet levels of this study and data on Feshbach resonances from various other sources. We recommend the derived potential function for further use. It can predict the deeply bound levels with an accuracy (about 50 MHz), comparable to that of the Fourier transform spectroscopy in [39]. The asymptotic levels are accurate on the order of a few MHz or better as their position is determined by the precisely measured location of Feshbach resonances. We improved the description of the large set of $^{87}\text{Rb}$ Feshbach resonances as compared to ref. [19] where the original calculation was based only on a few selected resonances and a derived asymptotic form of the two potentials. In [19] deviations as high as 2 G appeared and for example the resonances of asymptote $f_A = 1, m_A = 0 + f_B = 1, m_B = 1$ were all calculated systematically too high. In the present model these discrepancies disappear. The average deviation over all 46 resonances, given in [19–22], is about 0.15 G [50]. If one removes the R-dependence of the hyperfine coupling as given in Eq. 8 deviations in the order of 0.5 G appear varying according to the different $f$ levels which correlate to the Feshbach resonances. To improve the overall fit, one probably needs to include many-body effects of the collision process for detecting the resonances. The overall improvement of the long range behavior also allows the whole set of scattering lengths for the three isotopologues to be calculated. Table III gives a selection of these calculations. The error of these data will be in the last digit shown. These values are consistent with earlier publications but more precise and in general internally consistent between the isotopologues.

Our model will be valuable for our planned collision experiments of ultracold molecules which have to be prepared in well defined quantum states. The singlet-triplet mixing that we observe is of interest for a proposed precision experiment to measure the time dependence of the electron to proton mass ratio [11] (see also [9, 10]). The precision of future measurements would be mainly limited by the accuracy of the wave meter and could be improved by one or two orders of magnitude. Such a high precision could be used, e.g. to test the fundamental limits of the coupled-channel model, where we assume the validity of (1) the Born-Oppenheimer approximation, (2) using Zeeman terms with atomic parameters only, (3) a limited functional dependence in $R$ of the hyperfine and spin-spin interaction and (4) neglecting quadrupole hyperfine coupling.

Acknowledgments

We thank Marius Lysebo and Leif Veseth for model calculations to characterize the excited states $|\psi\rangle$. We thank Matthias Gerster for studying the simple Hamiltonian in Eq. (1). We acknowledge helpful predictions from Christiane Koch on the Franck-Condon overlap for the $|\psi\rangle - |\psi\rangle$ transition. This work was supported by the Austrian Science Fund (FWF) within SFB 15 (project part 17). E.T. thanks the cluster of excellence “QUEST” for support and the Minister of Science and Culture for providing a Niedersachenprofessur.

* These authors both contributed equally to this work.

[1] J. G. Danzl, E. Haller, M. Gustavsson, M. J. Mark, R. Hart, N. Bouloufa, O. Dulieu, H. Ritsch, and H.-C. Nägerl, Science 321, 1062 (2008).
[2] F. Lang, K. Winkler, C. Strauss, R. Grimm, and J. Hecker Denschlag, Phys. Rev. Lett. 101, 139005 (2008).
[3] K.-K. Ni, S. Ospelkaus, M. H. G. de Miranda, A. Pe`er, B. Neyenhuis, J. J. Zirbel, S. Kotochigova, P. S. Julienne, D. S. Jin, and J. Ye, Science 322, 5899 (2008).
[4] M. Viteau, A. Chotia, M. Allegrini, N. Bouloufa, O. Dulieu, D. Comparat, and P. Pillet, Science 321, 232 (2008).
[5] J. Deiglmayr, A. Grochola, M. Repp, K. Mörtlbauer, C.
Glick, J. Lange, O. Dulieu, R. Wester, and M. Weidemüller, Phys. Rev Lett. 101, 133004 (2008).
[6] P. Staunum, S. D. Kraft, J. Lange, R. Wester, and Matthias Weidemüller, Phys. Rev. Lett. 96, 023201 (2006).
[7] R. V. Krems, Int. Rev. Phys. Chem. 24, 99 (2005).
[8] R. V. Krems, Phys. Chem. Chem. Phys. 10, 4079 (2008).
[9] C. Chin, V. V. Flambaum, and M. G. Kozlov, New J. Phys. 11, 055048 (2009).
[10] T. Zelevinsky, S. Kotochigova and J. Ye, Phys. Rev. Lett. 100, 043201 (2008).
[11] K. M. Jones, E. Tiesinga, P. D. Lett, and P. S. Julienne, Rev. Mod. Phys. 78, 483 (2006).
[12] T. Köhler, K. Goral, and P. S. Julienne, Rev. Mod. Phys. 78, 1311 (2006).
[13] J. Weiner, V. S. Bagnato, S. Zilio and P. S. Julienne, Rev. Mod. Phys. 71, 1 (1999).
[14] L. E. E. de Araujo, J. D. Weinstein, S. D. Gensemer, F. Grim, and J. Hecker Denschlag, Phys. Rev. Lett. 100, 043202 (2008).
[15] K. M. Jones, E. Tiesinga, P. D. Lett, and P. S. Julienne, Phys. Rev. Lett. 100, 043202 (2008).
[16] J. Lozeille, A. Fioretti, C. Gabbanini, Y. Huang, H.K. Pechakis, D. Wang, P.L. Gould, E.E. Eyler, W.C. Stwalley, M. Aymar and O. Dulieu, Eur. Phys. J. D. 39, 261 (2006).
[17] B. Beser, V. B. Sovkov, J. Bai, E. H. Ahmed, C. C. Tsai, F. Xie, Li Li, V. S. Ivanov, and A. M. Lyrya, J. Chem. Phys. 131, 094505 (2009).
[18] M. Mudrich, Ph. Heister, T. Hippler, Ch. Giese, O. Dulieu, and F. Stienkemeier, Rev. Rev. A 80, 042512 (2009).
[19] A. Marte, T. Volz, J. Schuster, S. Dürr, G. Rempe, E. G. M. van Kempen, and B. J. Verhaar, Phys. Rev. Lett. 89, 283202 (2002).
[20] S. B. Papp, and C. E. Wieman, Phys. Rev. Lett. 97, 180404 (2006).
[21] J. L. Roberts, J. P. Burke, N. R. Clausen, S. L. Cornish, E. A. Donley, and C. E. Wieman, Phys. Rev. A 64, 024702 (2001).
[22] M. Erhard, H. Schmaljohann, J. Kronjäger, K. Bongs, and K. Sengstock, Phys. Rev. A 70, 031602 (2003).
[23] R. Wynar et al., Science 287, 1016 (2000).
[24] T. Volz, S. Dürr, S. Ernst, A. Marte, and G. Rempe, Phys. Rev. A 68 (2003).
[25] G. Thalhammer, K. Winkler, F. Lang, S. Schmid, R. Grimm, and J. Hecker Denschlag, Phys. Rev. Lett. 96, 050402 (2006).
[26] F. Lang, C. Strauss, K. Winkler, T. Takekoshi, R. Grimm, and J. Hecker Denschlag, Faraday Discussions 142, 271-282 (2009).
[27] F. Lang, Coherent transfer of ultracold molecules: From weakly to deeply bound, PhD Thesis, Institut für Experimentalphysik, Universität Innsbruck (2009).
[28] The width of the dark resonance scales as $\Omega_2$ if laser 2 is fixed on resonance and laser 1 is scanned.
[29] B. W. Shore, The Theory of Coherent Atomic Excitation (Wiley, New York), Sec. 10.4 (1990).
[30] In general, we define expectation values for the quantum numbers of an operator as $\sum \lambda_i |\langle e_i | \Psi \rangle|^2$, where $\lambda_i$ are the eigenvalues of the operator, $e_i$ are corresponding normalized basis vectors, and $| \Psi \rangle$ is the state.
[31] C. H. Townes, and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill Book Company (1955).
[32] G. Herzberg, Molecular Spectra and molecular structure - Vol I, D. Van Nostrand company (1950).
[33] T. M. Dunn, in Molecular Spectroscopy: Modern Research, (Eds. K. N. Rao, C. W. Mathews), p. 231, Academic Press (1972).
[34] S. Bize, Y. Sortais, M. S. Santos, C. Mandache, A. Clairon and C. Salomon, Europhys. Lett. 45, 558 (1999).
[35] O. Dulieu and P. S. Julienne, J. Chem. Phys. 103, 60 (1995).
[36] E. Tiesinga, C. J. Williams, and P. S. Julienne, Phys. Rev. A 57, 4257 (1998).
[37] M. Krauss, and W. J. Stevens, J. Chem. Phys. 93, 4236 (1990).
[38] A. Pashov, O. Docenko, M. Tamanis, R. Ferber, H. Knöckel and E. Tiemann, Phys. Rev. A 76, 022511 (2007).
[39] J. Y. Seto, R. J. LeRoy, J. Vergès, and C. Amiot, J. Chem. Phys. 113, 3067 (2000).
[40] F. H. Mies, and M. Raoult, Phys. Rev. A 62, 012708 (2000).
[41] T. Laue, E. Tiesinga, C. Samuelis, H. Knöckel, and E. Tiemann, Phys. Rev. A 65, 023412 (2002).
[42] G. Audi, A. H. Wapstra and C. Thibault, Nuclear Physics A 729, 337 (2003).
[43] E. Arimondo, M. Inguscio, and P. Violini, Rev. Mod. Phys. 49, 31 (1977).
[44] B. M. Smirnov and M. S. Chibisov, Zh.Eksp.Teor.Fiz. 48, 939 (1965)[Sov.Phys.JETP 21,624 (1965)]
[45] E. Tiemann, H. Knöckel, P. Kowalczyk, W. Jastrzebski, A. Pashov, H. Salami and A. J. Ross, Phys. Rev A 79 (2009).
[46] F. H. Mies, C. J. Williams, and M. Kraus J. Res. NIST, 101, 521 (1996).
[47] address of EPAPS
[48] In brief, using a three level model, where the Rabi frequency $\Omega_2$ is the only free parameter, we fit a line shape to the dark resonance.
[49] K. Winkler, F. Lang, G. Thalhammer, P. v. d. Straten, R. Grimm, J. Hecker Denschlag, Phys. Rev. Lett. 98, 043201 (2007).
[50] Three resonances reported by [49] were reassigned to the dark resonance [49].

$$\sum \lambda_i |\langle e_i | \Psi \rangle|^2$$