Spin-conservation propensity rule for three-body recombination of ultracold Rb atoms

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We explore the physical origin and the general validity of a propensity rule for the conservation of the hyperfine spin state in three-body recombination. This rule was recently discovered for the special case of $^{87}$Rb with its nearly equal singlet and triplet scattering lengths. Here, we test the propensity rule for $^{85}$Rb for which the scattering properties are very different from $^{87}$Rb. The Rb$_2$ molecular product distribution is mapped out in a state-to-state fashion using REMPI detection schemes which fully cover all possible molecular spin states. Interestingly, for the experimentally investigated range of binding energies from zero to $\sim$13 GHz x h we observe that the spin-conservation propensity rule also holds for $^{85}$Rb. From these observations and a theoretical analysis we derive an understanding for the conservation of the hyperfine spin state. We identify several criteria to judge whether the propensity rule will also hold for other elements and collision channels.

The particular mechanisms of chemical reactions often give rise to selection and propensity rules. While selection rules express strict exclusion principles for product channels, propensity rules specify which product channels are more likely to be populated than others [1, 2]. Since the early days of quantum mechanics a central question in reaction dynamics is whether composite spins are conserved. Wigner’s spin-conservation rule, e.g., states that the total electronic spin has a propensity to be conserved [3, 5]. The recent progress in the quantum state-resolved preparation and detection of ultracold atoms and molecules has now made it possible to experimentally explore spin conservation rules that also involve nuclear spins. In a recent study of bimolecular reactions of ultracold KRb molecules the conservation of the total nuclear spin was found [6, 7]. In a study on the final state distribution of three-body recombination of ultracold $^{85}$Rb atoms our group found a propensity for the conservation of the hyperfine state of the atom pair forming the molecule [8, 9]. More precisely, this spin propensity rule states that the angular momentum quantum numbers $F$, $f_a$, $f_b$, and $m_F = m_{f_a} + m_{f_b}$ are conserved in the reaction. Here, $f_a, f_b$ correspond to the total angular momenta of the two atoms $(a, b)$ forming the molecule, and $F = f_a + f_b$.

Formally, there is no selection rule that forbids spin exchange between all three atoms in the recombination process, and a corresponding change in the quantum numbers. In fact, recent calculations predict spin exchange to occur in three-body recombination of $^7$Li [10] and $^{39}$K [11, 12], although being suppressed for $^{87}$Rb [10]. In order to explain the observed spin propensity rule for $^{87}$Rb one can justifiably argue that $^{87}$Rb is special since here the singlet $(a_s)$ and triplet $(a_t)$ scattering lengths are nearly identical $(a_s \approx 90a_0, a_t \approx 99a_0$, where $a_0$ is the Bohr radius). This leads to a strong suppression of two-atom spin exchange reactions [13, 15].

In order to explore the validity of the spin propensity rule further, we investigate here, both experimentally and theoretically, three-body recombination of ultracold $^{85}$Rb atoms which have very different two-body scattering properties from $^{87}$Rb atoms. The singlet and triplet scattering lengths for $^{85}$Rb atoms are $a_s = 2720a_0$ and $a_t = -386.9a_0$ [16], respectively, and the three-body recombination rate constant $L_3$ for $^{85}$Rb is about four orders of magnitude larger than for $^{87}$Rb. Nevertheless, as a central result of our work, we find the spin propensity rule to also hold for $^{85}$Rb, within the investigated range of binding energies from zero to 13 GHz x h and the resolution of our experiment [17]. This result is corroborated by the fact that our measured product distributions are well reproduced by numerical three-body calculations based on a single-spin channel. The spin propensity rule that we find for $^{87}$Rb and $^{85}$Rb will also hold for other elements if certain conditions are met, which are formulated in the present work.

We carry out the measurements with an ultracold cloud of $2.5 \times 10^5$ $^{85}$Rb ground state atoms at a temperature of 860 nK and at near-zero magnetic field $B$. The atoms have spin $f = 2, m_f = -2$ and are trapped in a far-detuned optical dipole trap [18]. Three-body recombination produces weakly-bound molecules in the mixed singlet $^1\Sigma^+$ and triplet $^3\Sigma^+$ states [see Fig. 3(a)], which are coupled by hyperfine interaction [16]. We measure the yields of molecular products, observing a range of rovibrational states with vibrational and rotational quantum numbers $v, L_R$, respectively, from $v = -1$ to $-4$ [22] and from $L_R = 0$ to 6. A main result of our experiments is that we only find population in molecular states which are in the same spin state $F = 4, f_a = 2, f_b = 2$ (in short $F, f_a, f_b = 422$) as the reacting atom pair, although the investigated range of binding energies covers many bound states with different spin states. Because the two $^{85}$Rb atoms $(a, b)$ are identical bosons, the state $F, f_a, f_b = 422$ goes along with only having even angular momenta $L_R$ and a positive total parity.

We have extended our previous state-selective detection scheme [8] so that it now covers all symmetries of the dimer product state space, including spin triplet and singlet states with their respective $u/g$ symmetry. We apply two-step resonance-enhanced multiphoton ionization (REMPI), similar
to [21] [23] [26], but with a cw-laser. By two different REMPI pathways, (S) or (T), we probe product molecules via singlet or triplet character [see Fig. 1(a)]. Both schemes use identical photons for the two REMPI steps at wavelengths around 602.2 nm (see [18]). The intermediate states are deeply-bound levels of (2)1Σu+ and (2)3Πg for REMPI (S) and (T), respectively. When ions are produced via REMPI, they are directly trapped and detected in an eV-deep Paul trap which is centered on the atom cloud. Subsequently, elastic atom-ion collisions inflict tell-tale atom loss while the ions remain trapped. From the atom loss which is measured via absorption imaging of the atom cloud [8] [27] [28] the ion number can be inferred [18].

Figures 1(b) and (c) show REMPI spectra of Rb2 product molecules following three-body recombination, using path (S) and (T), respectively. Apart from three signals stemming from the photoassociation of two atoms (indicated by PA [29]), each resonance line of loss corresponds to a molecular product state. The photoassociation lines serve as references for the ∣f = 2, m_f = −2⟩ + ∣f = 2, m_f = −2⟩ asymptote corresponding to zero binding energy at about zero magnetic field. The vertical lines in Figs. 1(b) and (c) are predicted frequency positions for product states for the spin state F_{f_a}f_{b} = 422. These predictions are obtained from coupled-channel calculations for the X1Σg+ − a3Σu− complex [19]. Coincidences of predicted and observed lines allow for an assignment. As a consistency check for the assignment in Figs. 1(b) and (c) we make use of product states with L_R > 0 since these give rise to two resonance lines corresponding to the transitions towards J ′ = L_R ± 1. Indeed, the data in Figs. 1(b) and (c) confirm this consistency. Inspection clearly shows, that all experimentally observed spectral lines in Figs. 1(b) and (c) can be explained as signals from product molecules with the spin F_{f_a}f_{b} = 422. As an additional check for the line assignment, we show in [18] that our experimental spectra do not match up with molecular spin states other than F_{f_a}f_{b} = 422. This clearly indicates that the same spin propensity rule previously observed for 87Rb also holds for 85Rb.

For each product signal in the singlet REMPI path (S) we obtain a corresponding signal in the triplet REMPI path (T). This is because the spin state F_{f_a}f_{b} = 422, m_f = −4 has sizeable singlet (∼15%) and triplet (∼85%) admixtures. The spectra of Figs. 1(b) and (c) generally look different since the rotational constants differ for (2)1Σu+ (B_v = 289(1) MHz) and for (2)3Πg, 0+ (B_v = 389(2) MHz), see, e.g., [30]. The linewidths in Fig. 1(c) are typically on the order of 100 MHz (FWHM) which is larger than the typical linewidths in Fig. 1(b) of about 30 MHz. This is a consequence of the larger hyperfine splitting of the (2)3Πg state, which is not resolved in our measurements. In Fig. 1(c) at ν − ν_0 = 15.90 GHz there is a photoassociation signal which belongs to the 0− component of (2)3Πg. We show the corresponding REMPI spectrum in [18]. It exhibits the same molecular states as in Figs. 1(b) and (c).

We now carry out a more quantitative analysis where we compare the experimental signal strengths of the various REMPI paths and also compare them to theoretical calculations. For this, we measure the ion production rate for each assigned resonance line in Fig. 1 and Fig. S1 [18]. For a given REMPI path, the ion rate signal is expected to be proportional to the product molecule population rate, if we assume equal REMPI ionization efficiencies for the states. Our data show that this assumption is indeed fulfilled for most data points within the uncertainty limits of the recordings.

Figure 2 shows the extracted ion production rates γ of each molecular product state for the three REMPI paths (via (2)1Σu+, (2)3Πg, 0+ , and (2)3Πg, 0−). If a state is observed via
two or three different \( J' \) levels for a given path, we plot the average of the rates and mark the standard deviation from the mean with an error bar. In order to ease the comparison between the three data sets we have globally scaled the ion signals for the \( (2)^3\Pi_g \) 0⃗\( - \)g and \( (2)^3\Sigma_u^+ \) paths by a factor of 7.3 and 3.2, respectively, so that the signal bars for all REMPI paths in Fig. 2 are the same height for the state \( (v = -2, L_R = 4) \), see black arrow. These scaling factors compensate the differences in the ionization efficiencies of the different REMPI paths, which are due to the different singlet and triplet components of the product molecule as well as differences in the electric dipole transition moments, which are generally not very well known yet [31]. After the scaling the signals of the three paths for a given bound state are consistent over the set of detected product states.

In addition to the experimental data, we plot in Fig. 2 calculated channel rate constants \( L_3(v, L_R) \) for a temperature of 0.8 \( \mu \)K. The calculations use a single-spin model [18] which is similar to the one used in Ref. 8 in order to solve the three-body Schrödinger equation in an adiabatic hyperspherical representation [32,33]. For this, we use pairwise additive long range van der Waals potentials with a scattering length of \(-443a_0\) [34] for \(^{85}\text{Rb}\) and with a truncated number \( Z \) of \( L_R = 0 \) bound states (\( Z = 9 \) for Fig. 2). The calculated total recombination rate constant at 0.8 \( \mu \)K (including thermal averaging) is \( L_3 = 3.07 \times 10^{-25} \text{ cm}^3/\text{s} \) and is consistent with the values found in Ref. [35].

All data sets in Fig. 2 display the trend that the population of a molecular state due to three-body recombination typically decreases with increasing binding energy \( E_b \) of the product state, which is consistent with the work for \(^{87}\text{Rb}\) [8]. The overall agreement between theory and experiment in Fig. 2 is good, as the experimentally observed relative strengths of the signals for low \( L_R \) are in general well reproduced by the calculated recombination rates. This suggests that our single-spin model fully captures the characteristics of the three-body chemical reaction in the given parameter regime, which can be viewed as additional evidence for the spin propensity rule.

Based on our theoretical analysis, we conclude that the spin propensity rule in our experiment is a consequence of the following scenario. a) The reaction takes place at interparticle distances where the interactions of particles \( a \) and \( b \) (forming the molecule) with particle \( c \) are nearly spin-independent. b) In the investigated range all possible product molecules have quantum states with good quantum numbers \( F, f_a, f_b \). c) In the reaction region, the spin composition of the reacting pair \( a, b \) is essentially given by \( F f_a f_b = 422 \). As a consequence of conditions a), b) and c) the molecule formation is driven by mechanical forces from atom \( c \) while the spin state of the reacting pair is not affected.

To show that this scenario holds for our experiments, we first analyze the typical interparticle distances where the reaction occurs. Our numerical calculations [18] show that the formation of \(^{85}\text{Rb}_2\) molecules mainly takes place near a hyperradius \( R \approx 1.5r_{vdw} \), extending from \( R \approx 1.1r_{vdw} \) to \( 2r_{vdw} \). Here, \( r_{vdw} = (2\mu C_6/h^2)^{1/4} \approx 82a_0 \) denotes the van der Waals length for Rb, and \( \mu \) and \( C_6 \) are the reduced mass and the van der Waals coefficient of the two-particle system, respectively. The hyperradius \( R \) describes the characteristic size of the three-body system and is given by \( R^2 = (\vec{r}_a - \vec{r}_b)^2 / d^2 + d^2(\vec{r}_a - (\vec{r}_a + \vec{r}_b)/2)^2 \), where \( \vec{r}_i \) is the location of particle \( i \) and \( d^2 = 2/\sqrt{3} \). The fact that the reactions occur at these large \( R \) can be understood within the framework of the adiabatic hyperspherical representation, where an effective repulsive barrier for the three-body entrance channel forms at a hyperradius of about \( R = 1.7r_{vdw} \) [18,36].

We now consider the formation of a molecule state with a size \( \lesssim r_{vdw} \approx 0.6r_{vdw} \). Only for such a state can spin components other than \( F f_a f_b = 422 \) be substantial (for more details see [18]). Here, \( r_{vdw} = (C_6/E_{vdw})^{1/6} \) is the hyperfine radius and \( E_{vdw} = 3.04 \text{GHz} \times h \) is the atomic hyperfine splitting. Given the hyperradius \( R > 1.1r_{vdw} \) and the interparticle distance \( r_{ab} \equiv |\vec{r}_a - \vec{r}_b| < r_{vdw} \), the distances of particle \( c \) to the others must be \( r_{ca}, r_{cb} > 0.6r_{vdw} \). Since the interaction between two Rb atoms is essentially spin-independent for distances \( \gtrsim 0.25r_{vdw} \), this validates point a) of the scenario described above. Concerning point b), our coupled-channel calculations show that the weakly-bound molecular states up to a binding energy of about 50GHz \( \times h \) have almost pure spin states \( F f_a f_b \). This can be explained by the fact that the \(^{85}\text{Rb}\) triplet and singlet scattering lengths are large in magnitude. For \(^{85}\text{Rb}\), where these scattering lengths are of opposite sign, this leads to a near energetical degeneracy of the triplet vibrational levels \( v_T \) with the singlet vibrational levels \( v_S = v_T - 1 \) [37,38]. Since, in addition, the singlet and triplet vibrational wavefunctions are very similar at long range, the interaction between the two atoms is essentially spin-independent. As a consequence the atomic hyperfine interaction of each atom is essentially unperturbed, which leads to the atomic hyperfine
Subsequent coupling of structure with the quantum numbers $f$ for various binding energies (see text). The scattering state therefore shares the relatively pure singlet and triplet components. Shown are the three spin families with $F = 4$ which correlate with the states $F_f f_b = 422, 423, 433$ at the $E_h = 0$ threshold. Red dashed arrows are guides to the eye and indicate the change of each family’s spin character with increasing binding energy. The norm of the 422 spin component is presented in parentheses for the 423 and 422 families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy. The norm of $F f$ with the states $r = 422$ families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy. The norm of $F f$ with the states $r = 422$ families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy. The norm of $F f$ with the states $r = 422$ families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy. The norm of $F f$ with the states $r = 422$ families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy. The norm of $F f$ with the states $r = 422$ families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy. The norm of $F f$ with the states $r = 422$ families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy. The norm of $F f$ with the states $r = 422$ families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy. The norm of $F f$ with the states $r = 422$ families. For the 433 family the 422 norm is about 1% for the family’s spin character with increasing binding energy.
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[18] See Supplementary Material at ..., which includes Refs. [41–44] for further information about the experimental setup and methodology, the theoretical model, additional REMPI data, as well as aspects and tests of the spin propensity rule.

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SUPPLEMENTAL MATERIAL

Ultracold atoms set-up

The ultracold $^{85}$Rb atoms are initially prepared in the spin state $f = 2, m_f = -2$ of the electronic ground state. This state is stable in two-body collisions due to energetic closure of other atomic exit channels and due to small dipolar relaxation rates. Indeed, our coupled-channel calculations have verified that the two-body spin-relaxation rate constants for $^{85}$Rb remain below $10^{-14} \text{cm}^3/\text{s}$ when the magnetic field is not near a Feshbach resonance. The scattering length for the collision of two $f = 2, m_f = -2$ atoms is $a = -460 a_0$.

In our set-up the atoms are trapped in a far-detuned optical dipole trap with trapping frequencies $\omega_{x,y,z} = 2\pi \times (156, 148, 18) \text{ Hz}$. The optical dipole trap operates at a wavelength of about 1064-nm.

REMPI

For REMPI we use a laser wavelength around 602.2 nm. The laser light is either provided by a cw dye laser (Matisse, Sirah Lasertechnik GmbH) or an optical parametric oscillator (C-Wave, Hübnner GmbH). Each laser is stabilized to a cavity and has a short-term linewidth of less than 1 MHz. Longer term drifts are compensated by a lock to a wavelength meter and we have a shot-to-shot frequency stability on the order of term drifts are compensated by a lock to a wavelength meter and has a short-term linewidth of less than 1 MHz. Longer

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Ion number calibration

For each molecular resonance line in the spectra of Fig. 1 and Fig. S1 we have measured the ion production rate in our experiment. For this, we tune the ionization laser onto a given resonance and turn it on for a short enough pulse time so that only a few ions ($< 20$) are produced. We are then in a regime where the ion number grows linearly with time (see inset of Fig. S1 for a typical measurement). Afterwards we count the number of ions by inserting them into a fresh atom cloud with $2.5 \times 10^5$ atoms. After an interaction time of 500 ms, during which the ions inflict atom loss due to (mostly) elastic atom-ion collisions, we measure the remaining number of atoms with absorption imaging. Using the calibration curve in Fig. S2, we can convert the measured atom fraction into an ion number. Dividing the ion number by the pulse time we obtain the ion production rate.

The calibration curve was obtained as follows. Initially, the ion trap and the optical dipole trap are spatially separated from each other so that the atoms cannot collide with the ions. A known number of laser-cooled $^{138}$Ba$^+$ ions in a range between 1 to about 40 is prepared in the Paul trap. The cold ions form an ion crystal in the trap and are counted with single-particle resolution after fluorescence imaging. In parallel, we prepare a $^{85}$Rb atom cloud in the crossed optical dipole trap. Next, the centers of the ion and atom traps are overlaid, immersing the Ba$^+$ ions into the atom cloud. Subsequently, the Ba$^+$ ions can undergo reactions with the Rb atoms, such as, e.g., charge
FIG. S1. REMPI spectrum via the triplet path (T) with intermediate state \((2^3\Pi_g, 0_g^-, \nu' = 10).\) The remaining atom fraction \(N/N_0\) is plotted as a function of the REMPI laser frequency \(v.\) \(v_0 = 497847.828\) GHz is the resonance frequency for photoassociation (PA) towards \((2^3\Pi_g, 0_g^-)\) \((J' = 0).\) A second photoassociation line for a transition towards \((2^3\Pi_g, 0_g^-)\) \((J' = 2)\) is located at around \(\nu - v_0 = 2.4\) GHz. The vertical lines are predicted possible line positions of molecular states. If observed they are purple (0\(g^-\)) or black (0\(g_-\)), if unobserved they are gray. The lines involving 0\(g_-\) are marked with the vibrational quantum number \(v.\) The rotational quantum number \(L_R\) and the intermediate level \(J'\) are given by the linestyle and the plot symbols, respectively (see legends).

FIG. S2. Atom loss due to elastic collisions with \(N_i\) ions (predominantly \(\text{Rb}^+).\) Shown is the remaining atom fraction \(N/N_0\) of the atom cloud after 500 ms of atom-ion collisions with \(N_i\) ions previously prepared in the Paul trap. The dashed line is the fit function \(N/N_0 = (\frac{N_i}{\alpha})^\beta\) with the fit parameters \(\alpha = 1.4\) and \(\beta = -10.1.\) The inset is a typical measurement of the ion number as a function of the REMPI laser pulse duration. For the given example, the REMPI laser frequency is set to resonantly excite the molecular state \((v, L_R) = (-1, 2)\) towards the \((2^3\Pi_g, 0_g^-, \nu' = 10, J' = 2)\) intermediate state. The dashed line is a linear fit to the data.

FIG. S3. Total three-body recombination rate \(L_3\) (black solid line) and corresponding partial rates for the six most weakly-bound molecular states currently observed, \((v, L_R) = (-1, 2), (-1, 0), (-2, 6), (-2, 4), (-2, 2)\) and \((-2, 0),\) as well as \((-3, 0)\) and \((-4, 0),\) calculated with a two-body interaction model supporting 5 s-wave bound states. These results indicate that recombination is likely to occur at \(R > 1.5r_{vdW}\) due to the presence of a repulsive barrier on the inclusion collision channel (see text) and for \(R > 1.5r_{vdW}\) due to the decrease of the hyperradial inelastic couplings with \(R\). After a long interaction time of 2s we are predominantly left with \(\text{Rb}^+\) ions, as confirmed by mass spectrometry. Although these ions can have high kinetic energy they are still confined in the eV-deep Paul trap, i.e., the initial number of trapped ions is conserved. Afterwards, the ion trap and the optical dipole trap are separated again from each other, the old atom cloud is discarded and a new atom cloud (with \(2.5 \times 10^{10}\) atoms) is prepared. The ions are immersed into the new atom cloud for 500 ms and atom-ion collisions inflict again atom loss. Figure S2 shows the remaining atom fraction \(N/N_0\) as a function of initial ion number \(N_i.\) The dashed line is a fit with the empirically-found function \(N/N_0 = (\frac{N_i}{\alpha + 1})^\beta.\) Here, \(\alpha\) and \(\beta\) are fit coefficients.

### Three-body model for \(^{85}\text{Rb}\) atoms

Our three-body calculations for \(^{85}\text{Rb}\) atoms were performed using the adiabatic hyperspherical representation \([32, 33]\) where the hyperradius \(R\) determines the overall size of the system, while all other degrees of freedom are represented by a set of hyperangles \(\Omega.\) Within this framework, the three-
body adiabatic potentials $U_\alpha$ and channel functions $\Phi_\alpha$ are determined from the solutions of the hyperangular adiabatic equation:

$$\left[\frac{\Lambda^2(\Omega)+15/4}{2\mu R^2} + \sum_{i<j} v(r_{ij})\right] \Phi_\alpha(R;\Omega) = U_\alpha(R) \Phi_\alpha(R;\Omega),$$

(1)

which contains the hyperangular part of the kinetic energy, expressed through the grand-angular momentum operator $\Lambda^2$ and the three-body reduced mass $\mu = m/\sqrt{3}$. To calculate the three-body recombination rate we solve the hyperradial Schrödinger [33],

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + U_\alpha(R) \right] F_\alpha(R) + \sum_{\alpha'} W_{\alpha\alpha'}(R) F_{\alpha'}(R) = E F_\alpha(R),$$

(2)

where $\alpha$ is an index that labels all necessary quantum numbers to characterize each channel, and $E$ is the total energy. From Eq. (2) we determine the $S$-matrix and the recombination rate $L_3$ [33].

In this present study, the interaction between $^{85}$Rb atoms is modeled by a potential similar to that used in Ref. [38], and given by a modified Lenard-Jones potential,

$$v(r) = -\frac{C_6}{r^6} \left( 1 - \frac{\lambda^6}{r^6} \right) - \left( \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right) [f_\lambda(r)]^2 [f_\lambda(r)]^{12},$$

(3)

where $C_6 = 4710.431E_h a_0^6$, $C_8 = 576722.7E_h a_0^8$, and $C_{10} = 75916271E_h a_0^{10}$, are the van der Waals dispersion coefficients from Ref. [16]. Here, $f_\lambda(r) = \tanh(2r/\lambda)$ is a cut-off function that suppresses the divergence of the $C_8$ and $C_{10}$ interaction terms for vanishing interatomic distance $r$. We can adjust the value of $\lambda$ to have different numbers of diatomic bound states supported by the interaction, while still reproducing the value of the background scattering length $a_{bg} = -443a_0$ [34]. Our calculations were performed using $\lambda = 20.72577414766491a_0$, producing 9 $s$-wave ($L_R = 0$) bound states, and a total of 101 bound states including higher partial-wave states, $L_R > 0$. Our numerical calculations for three-body recombination through the solutions of Eq. (2) have included up to 200 hyperspherical channels leading to a total rate converged within a few percent. The calculated total recombination rate constant at $0.8 \mu K$ (including thermal averaging) is $L_3 = 3.07 \times 10^{-25}$ cm$^3$/s and is consistent with the values found in Ref. [35].

In order to gain more insight on how three-body recombination occurs within the hyperspherical representation we introduced an artificial hyperradial hard-wall at $R = R_{hw}$ and performed recombination calculations for various values of $R_{hw}$. The hard-wall prevents any flux into the range $R < R_{hw}$ and therefore reactions in this range are not possible. By analyzing how the total and partial reaction rates change as a function of $R_{hw}$ one can infer at what hyperradial $R_\lambda$ reactions dominantly occur. Figure S3 shows the total rate $L_3$ (black solid line) and the partial rates for some of the currently observed molecular states, $(v, L_R) = (-4, 0)$ (b). A point on the $\theta-\varphi$ hyperangular plane specifies the geometry of the three-atom system. The regions within the circles marked by dashed lines, correspond to geometries for which two of the atoms are found at distances $r_{ij} \leq r_{vdW}$ and $r_{ij} \leq r_{hd}$, respectively, while the third atom is further away.

![FIG. S4. Hyperangular probability density, $|\Phi_\alpha(R; \theta, \varphi)|^2 \sin(2\varphi)$](image)

At $R = 1.593 r_{vdW}$ for the initial collision channel (a) and the molecular product state $(v, L_R) = (-4, 0)$ (b). A point on the $\theta-\varphi$ hyperangular plane specifies the geometry of the three-atom system. The regions within the circles marked by dashed lines, correspond to geometries for which two of the atoms are found at distances $r_{ij} \leq r_{vdW}$ and $r_{ij} \leq r_{hd}$, respectively, while the third atom is further away.
peaking of the reaction rates at around \( R \approx 1.5 r_{vdW} \) in Fig. S3 can be explained as a consequence of a repulsive barrier in the hyperspherical effective potential of the entrance channel at \( R \approx 1.7 r_{vdW} \). Such a barrier was first identified in Ref. [36] where it occurred at \( R \approx 2 r_{vdW} \) for \( a = \pm \infty \).

We now analyze the geometric characteristics of the three-atoms system in the region where recombination is most likely to occur in order to identify which type of coupling is dominating the inelastic transitions. Figure S4 shows the hyperangular probability density at \( R = 1.593 r_{vdW} \) in terms of the hyperspherical channel functions \( \Phi_n \) and hyperangles \( \theta \) and \( \phi \) as: \( \Phi_n(R;\theta,\phi)^2 \sin(2\theta) \) (see Ref. [36]). Each point in the \( \theta-\phi \) hyperangular plane corresponds to a specific geometry of the three-atom system. In particular, the regions within the dashed half-circles represent geometries where two of the atoms are found at a distance \( r_{ab} \leq r_{vdW} \) and \( r_{ab} \leq r_{hd} \), respectively, and the third atom remains at distances \( r_{ca}, r_{cb} > r_{hd} \) (i.e., \( r_{ci} \approx 0.71 r_{vdW} \) and \( r_{ci} \approx 1.2 r_{vdW} \), respectively). In Fig. S4(a) we show the probability density for the initial collision channel, which indicates that the most likely configuration is where all three atoms are located at distances typically larger than 1.7 \( r_{vdW} \). In contrast, the probability density for the target molecular states is pronounced inside the small circle. As an example, Fig. S4(b) shows the probability density for \( (v_L_R) = (-4, 0) \). In order to produce this state, the two atoms forming the bound state obviously need to be closer than \( r_{hd} \) and the third atom is at interparticle distances \( r_{ab} > r_{hd} \). For a spin flip to happen during the reaction, the two atoms forming the molecule must be at a distance \( r_{ab} < r_{hd} \) and the wavefunctions of either the two-body scattering state or the two-body target bound state must have a sizeable spin admixture. In the range of binding energies discussed here for \(^{85}\text{Rb}\) these admixtures are on the %-level and therefore quite small. The admixtures are not shown in Fig. S4.
Characteristics of collisions at large distance

The interaction between two Rb atoms is effectively spin-independent for interparticle distances \( r_{ij} \equiv |\vec{r}_i - \vec{r}_j| \gtrsim 0.25 r_{vdW} \). This is because at these distances the exchange splitting between the electronic singlet and triplet ground state potentials is smaller than the atomic hyperfine splitting \( E_{hf} = 3.04 \text{GHz} \times h \). As a consequence the atomic hyperfine states are only weakly perturbed by the exchange interaction and therefore essentially remain eigenstates in this realm. In other words the exchange interaction is not strong enough to decouple the atomic hyperfine spins and flip them.

Next, we consider the low-energy collision of two \( f = 2, m_f = -2 \) Rb atoms, corresponding to the channel \( F_{fa}F_{fb} = 422 \). At vanishing magnetic field and neglecting dipolar relaxation processes, \( F \) and \( m_F \) are conserved throughout the collision. At a close enough distance \( < 0.25 r_{vdW} \) spin exchange interaction, however, can admix the spin states \( F_{fa}F_{fb} = 423, 433 \) (For an overview of all spin channels of two colliding ground state \(^{85}\text{Rb} \) atoms see [44]). Interestingly, this admixture is restricted to distances \( r_{ab} < r_{vdW} \approx 0.6 r_{vdW} \) due to energetic closure of the \( F_{fa}F_{fb} = 23, 33 \) scattering channels at larger distances. For \( m_F = -4 \), the channel \( F_{fa}F_{fb} = 422 \) is the lowest in energy. The hyperfine distance \( r_{vdW} = (C_6/E_{vdW})^{1/6} \) is the distance at which the potential curve of channel \( F_{fa}F_{fb} = 23 \) crosses the collision energy (which approximately corresponds to the asymptotic energy of the 422 channel). This crossing is also relevant in another regard. It effectively limits the size of molecular bound states of the spin channels \( F_{fa}F_{fb} = 23, 33 \) which are energetically located below the \( F_{fa}F_{fb} = 422 \) entrance channel to be \( < r_{vdW} \approx 0.6 r_{vdW} \).

We now consider a three-body collision of three \( f = 2, m_f = -2 \) atoms and assume the hyperradius to be \( R > 1.1r_{vdW} \). Using the expression \( R^2 = (\vec{r}_i - \vec{r}_j)^2/d^2 + d^2(\vec{r}_i - (\vec{r}_a + \vec{r}_b)/2)^2 \), where \( \vec{r}_i \) is the location of particle \( i \) and \( d^2 = 2/\sqrt{3} \), we calculate that for \( R > 1.1 r_{vdW} \) at least one of the three atoms, say \( c \), has distances \( r_{ca}, r_{cb} > 0.6 r_{vdW} \) from both other atoms. This is outside the distance range \( r_{ca}, r_{cb} < r_{vdW} \approx 0.6 r_{vdW} \) for atom \( c \) to exhibit a spin admixture. Therefore, atom \( c \) should have a pure spin state \( f = 2, m_f = -2 \), even if it had possibly undergone spin exchange interaction in a previous collision with one of the other two atoms. Reciprocally, we can conclude that the two other colliding atoms \( a \) and \( b \) must be in the collision channel \( F_{fa}F_{fb} = 422 \). Thus, at a hyperradius \( R > 1.1 r_{vdW} \) the three-body system can be effectively decomposed (with respect to spin) into a two-body collision of two \( f = 2, m_f = -2 \) atoms and a third atom which is spin-wise only a spectator.

Spin composition of \(^{87}\text{Rb}_2\) molecules

Figure S5 shows the binding energy and the spin composition of weakly-bound \(^{87}\text{Rb}_2\) molecules. For \(^{87}\text{Rb}_2\) the ratio \( \rho \) is given by \( \rho = |E_T(v) - E_S(v)|/E_{vdW} \). It becomes > 1 for binding energies \( E_b \gtrsim 100 \text{GHz} \times h \). Around \( \rho = 1 \) a major change in the spin composition of the spin families occurs.

Tests of the spin propensity rule

In the spectra of Fig. 1 and Fig. S1 we showed that our observed lines match with the calculated positions of molecular states with \( F_{fa}F_{fb} = 422 \). For the sake of completeness we show here with a few examples, that our data do not match with the calculated spectra of other spin families. Figure S6(a) shows a section of the spectrum in Fig. 1(b) together with calculated positions for product molecules with \( f_a f_b = 23 \) and 33. The positions are indicated by vertical red and purple lines, respectively. Each of the bound states with different \( F \) (from 0 to 6) is plotted separately in vertical direction. Clearly, there is no convincing match between these and the experimental lines within the detection limit. The observed lines only match calculated resonance frequency positions for molecules with \( F_{fa}F_{fb} = 422 \). In Fig. S6(b) we zoom in further into the spectrum shown in Fig. S6(a) and check for molecules with \( F_{fa}F_{fb} = 022 \) and \( F_{fa}F_{fb} = 222 \). Again, the observed signals only match in a convincing way for \( F_{fa}F_{fb} = 422 \).