Are ultracold molecular collisions sticky?

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Understanding and controlling collisions is crucial to the burgeoning field of ultracold molecules. All experiments so far have observed fast loss of molecules from the trap. However, the dominant mechanism for collisional loss is not well understood when there are no allowed 2-body loss processes. Here we experimentally investigate collisional losses of nonreactive ultracold $^{87}$Rb$^{133}$Cs molecules, and compare our findings with the ‘sticky collision’ hypothesis that pairs of molecules form long-lived collision complexes. We demonstrate that loss of molecules occupying their rotational and hyperfine ground state is best described by second-order rate equations, consistent with the expectation for complex-mediated collisions, but that the rate is lower than the limit of ‘universal loss’. The loss is insensitive to magnetic field but increases for excited rotational states. We demonstrate that dipolar effects lead to significantly faster loss for an incoherent mixture of rotational states.

A growing number of experiments now produce ground-state polar molecules at ultracold temperatures, either by associating pairs of atoms [11] or by direct laser-cooling of molecules [9] [10]. These experiments offer an exciting new platform for the study of ultracold dipolar gases [11] [15] and quantum-state-controlled chemistry [16] [19]. For molecules produced by association, the sample densities are sufficiently high that molecular collisions are important and measurable. Yet a proper understanding of ultracold molecular collisions remains elusive.

For ultracold atomic systems, a detailed understanding of collisions has been developed through decades of research comparing theory and experiment [20] [21]. In particular, the control of interactions through intra-species magnetic Feshbach resonances [21] [24], with quantitative calculations of the scattering length, has proved crucial. For example, it has allowed study of the BCS crossover in Fermi gases [25] [31] and of Efimov physics [32] [42]. A detailed understanding of collisions will be equally crucial in future experiments with ultracold molecular gases.

There has been relatively little comparison of experiment and theory for molecular collisions. Many alkali dimers can undergo exoergic two-body exchange reactions of one or more of the types

\[2XY \rightarrow X_2 + Y_2; \]
\[2XY \rightarrow X_2Y + Y; \]
\[2XY \rightarrow X + XY_2. \]

(1)

Ultracold collisions between such molecules have been studied experimentally in KRB [15] [33] [44], NaLi [7], and triplet Rb$_2$ [45]. Collisional loss was found to occur with high probability for molecular pairs that reach short range, and was attributed to the reactions [1]. However, there are other alkali dimers, such as NaRb and RbCs in their vibronic ground states, for which all the reactions [1] are energetically forbidden [46]. Surprisingly, these also show high collisional loss rates. For example, Ye et al. [47] compared the loss rate for NaRb molecules in the ground and first-excited vibrational states, and found high loss and heating rates regardless of the energetics of the reactions.

One possible mechanism for fast losses of chemically stable species has been proposed by Mayle et al. [48] [49]. They argue that the large number of rovibrational states available supports a dense manifold of Feshbach resonances. Resonant collisions may form long-lived two-molecule collision complexes. A further collision between a complex and a molecule can then lead to loss of all three molecules from the trap. This may produce second-order kinetics even though the loss is three-body in nature. Nevertheless, the three-body loss is effectively enhanced by the long lifetime of the complexes. We refer to this as the ‘sticky collision’ hypothesis.

The lifetime $\tau$ of a collision complex is related to the resonance width $\Gamma$ by $\tau = h/\Gamma$. The model of Mayle et al. assumes that the mean width is $\langle \Gamma \rangle = N_o/2\pi \rho$, where $\rho$ is the density of states and $N_0$ is the number of open channels for the ‘free’ molecular pair. This is based on Rice-Ramsperger-Kassel-Marcus (RRKM) theory [50] and effectively assumes that the motion is ergodic, i.e. that energy is fully randomised in the complex. For collisions of RbCs in the rovibrational ground state, $N_o = 1$ and the predicted density of states is $\rho/k_B = 942 \mu K^{-1}$ ($\rho/\mu_{\text{mag}} = 368 \text{ G}^{-1}$) [49]; this gives a sticking lifetime of 45 ms.

In this work, we test the model of Mayle et al. by measuring loss from an optically trapped sample of ground-state RbCs molecules. These molecules are chemically stable against all available two-body atom-exchange reactions [46], yet fast losses are still observed. We demon-
strate that the loss is best described by a rate equation that is second-order in the density. We investigate the temperature dependence of the loss in the rotational and hyperfine ground state, and compare our results to a single-channel model that uses an absorbing boundary condition to take account of short-range loss \[51, 52\]. We find a significant difference between the measured loss rates and those expected in the universal limit, in which all two-body collisions that reach short range lead to loss. We then increase the internal energy of the molecule, both by varying the magnetic field and by preparing the molecules in excited rotational and/or hyperfine states, and observe similar loss rates. Finally, we prepare the molecules in an incoherent mixture of ground and first-excited rotational states. In this mixture we observe a much faster loss than for molecules in a single state.

Taken together, our measurements support the sticky collision hypothesis, but with a rate lower than predicted by the full model of Mayle et al. \[49\]. This may arise from a breakdown of ergodicity, manifested as an average width smaller than predicted by RRKM theory and perhaps due to a geometrical restriction on complex formation.

**RESULTS**

**Measuring loss due to molecule-molecule collisions**

Our experiments are performed with a gas of \(X^1\Sigma^+\) RbCs molecules, initially occupying the vibrational and spin-stretched hyperfine ground state \(|N = 0, M_N = 0, m^\text{Rb} = 3/2, m^\text{Cs} = 7/2\) at a magnetic field of 181.5 G. Here, \(N\) is the rotational quantum number with projection \(M_N\) along the quantization axis, and \(m^\text{Rb}\) and \(m^\text{Cs}\) are the atomic nuclear spin projections. The molecules are confined to an optical dipole trap (ODT) with typical initial temperature 1.5(1) \(\mu\)K and peak density of 1.9(2) \(\times 10^{11}\) cm\(^{-3}\). We observe loss of molecules as a function of hold time in the ODT as shown in Fig. 1. A molecule is considered ‘lost’ either if it is ejected from the trap or if it is in a state other than that in which it was prepared (including a complex).

To characterize the dominant loss mechanism, we model the rate of change of density \(n\) as \(\dot{n}(r, t) = -k_{\gamma} n(r, t)^{\gamma}\), where the power of the density \(\gamma = 1, 2, 3\) corresponds to losses where the rate-determining step is a one-, two-, or three-body process, respectively. We numerically solve the coupled rate equations

\[
\dot{N}_{\text{mol}}(t) = -k_\gamma C^{(\gamma-1)} \left( \frac{N_{\text{mol}}(t)^\gamma}{\gamma^{3/2}T(t)^{(3/2)(\gamma-1)}} \right),
\]

\[
T(t) = k_\gamma C^{(\gamma-1)} \left( \frac{2 - \gamma}{2\gamma} \right) \left( \frac{N_{\text{mol}}(t)^{-\gamma-1}}{\gamma^{3/2}T(t)^{(\gamma-5)/2}} \right),
\]

(derived in Supplementary Note 1) and fit the variation in number with \(\gamma\) and \(k_\gamma\) as free parameters. Here, \(N_{\text{mol}}(t)\) is the number of molecules remaining in the initial state, \(T(t)\) is the temperature of the remaining distribution, and \(C = (m\omega^2/2\pi k_B)^{3/2}\), where \(m\) is the mass of the molecule and \(k_B\) is the Boltzmann constant. In deriving Eq. 2 it is assumed that the molecules remain in thermal equilibrium and that \(k_\gamma\) is independent of temperature. We fix the initial temperature, and hence the initial density, in the fitting. An example result is shown in Fig. 1. We find an optimal value of \(\gamma = 2.07(7)\) (reduced chi squared \(\chi^2_{\text{red}} = 0.998\)), shown by the solid black line, suggesting that the loss is governed by a two-body process. Fits with \(\gamma\) fixed at 1.2 and 3 have \(\chi^2_{\text{red}} = 22.9, 1.27\) and 10.4 respectively; in all future fitting we therefore constrain the fits such that \(\gamma = 2\). The results shown yield a two-body inelastic loss rate coefficient \(k_2 = 4.8(6) \times 10^{-11}\) cm\(^3\) s\(^{-1}\).

To confirm the second-order behavior, we explore the initial loss rate as a function of the starting density, by varying the number of molecules with the temperature and trap frequencies fixed. To extract the loss rate, we fit the first 0.2 s of molecule loss with a linear function to extract the gradient. The variation of the initial loss rate

![FIG. 1: Loss of ground state molecules. Collisional loss of molecules in \(|N = 0, M_N = 0, m^\text{Rb} = 3/2, m^\text{Cs} = 7/2\) with initial temperature of 1.5(1) \(\mu\)K and peak density 1.9(2) \(\times 10^{11}\) cm\(^{-3}\). Each result is an average of at least 5 experimental runs, with standard error shown. The solid black line shows a fit to the coupled rate equations given in Eq. 2 with uncertainty in \(\gamma\) shaded. The dashed lines show fits to the data with fixed \(\gamma = 1, 2, 3\) corresponding to one-, two-, and three-body loss respectively. Inset: Density dependence of the initial loss rate on a log-log scale. The solid line is a linear fit, while the dashed lines indicate the expectations for one-, two-, and three-body loss.](image-url)
known as the universal limit, the loss is independent of \( k \). The universal rate coefficient at zero temperature is \( \frac{C_6}{s} \), which is caused by the dispersion interaction. For RbCs in its rovibrational ground state, \( C_6 = 141\,000\, E_h a_0^6 \), which gives \( \bar{a} = 233\, a_0 \) and \( k_{2\text{univ}}(0) = 1.79 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \) at zero temperature. Our model [52] carries out QDT using Gao’s analytic wavefunctions for a pure \( R^{-6} \) potential [51, 55], which account for reflection from the long-range potential. It allows variation of the loss parameter \( y \) and includes multiple partial waves, so gives the complete energy dependence of the loss rates, rather than just the leading term as in ref. [51]. We calculate the thermally averaged rate coefficient, \( k_2(T) = \int_{\text{kin}} D(E) dE \), where \( D(E) = \int_{\text{kin}} \exp(-E/k_B T) dE \).

Figure 2 shows a contour plot of the thermally averaged loss rate coefficient \( k_2(T) \) for ground-state \( \text{RbCs}^+\text{RbCs} \) at 1.5 \( \mu\)K. Finite-temperature effects are important: In the universal limit, \( y = 1 \), the rate coefficient approaches 9.93 \times 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \), which is nearly a factor of two lower than the zero-temperature value. When \( y < 1 \), the loss may be either lower or higher than the universal limit, depending on \( \delta^s \). Around \( \delta^s = \pi/8 \), resonant s-wave scattering enhances the magnitude of the wavefunction at short range and causes a broad enhancement in the loss. Around \( \delta^s = 5\pi/8 \) there is a narrower band of enhanced rates due to a d-wave shape resonance. Shape resonances for higher partial waves exist in \( k_2(E) \) [52], but are washed out by thermal averaging in \( k_2(T) \).

Contours corresponding to the measured \( k_2 \) at 1.5 \( \mu\)K and its 1\( \sigma \) confidence limits are shown in Fig. 2. There is a band of parameter space that gives loss rates in agreement with experiment. The largest part of this band is in the region \( 0.2 < y < 0.4 \), but lower values of \( y \) are possible in the region of large scattering length around \( \delta^s = \pi/8 \). Nevertheless, the region of agreement with the experiment is entirely \( y < 0.4 \), showing that this system is significantly removed from the universal limit.

**Temperature dependence**

The temperature dependence of the loss rate contains important additional information. Figure 3 shows the calculated thermally averaged rate coefficients, as a function of temperature, for different values of the short-range phase \( \delta^s \); for each phase, the loss parameter \( y \) is chosen to match the experimental rate coefficient at \( T = 1.5 \, \mu\)K. It may be seen that the form (and even the sign) of the temperature dependence varies substantially with \( \delta^s \).

We measure loss with a range of starting temperatures from 0.85(5) \( \mu\)K to 3.3(3) \( \mu\)K. Including temperature dependence allows us to fit the short-range phase as well as the loss parameter \( y \). The best-fit parameters are \( y = 0.26(3) \) and \( \delta^s = 0.56_{-0.05}^{+0.07} \). The fitted loss rate is shown as the green line in Fig. 3 with uncertainty given by the shaded region. This gives us our first indication of the scattering length for \( \text{RbCs}^+\text{RbCs} \) collisions; the fitted \( \delta^s \) corresponds to 231 < \( a < 319 \, a_0 \).

**Magnetic field dependence**

The single-channel model has no explicit dependence on magnetic field, but at fields below 98.8 G the ini-
Collisions in rotationally excited states

We also consider loss of molecules in rotationally and hyperfine excited states \[56\]. We have measured loss rate coefficients at 1.5 \( \mu \)K for two hyperfine-excited states with \( N = 0 \), two states with \( N = 1 \) and one state with \( N = 2 \). The universal rate changes between states because of different rotational contributions to \( C_6 \), as shown in Supplementary Table 1. The rate coefficients as a fraction of the universal rate are shown in Fig. 3, labelled by \( y, \delta^* \) that follow the solid black line in Fig. 2.

Potential state is no longer the lowest in energy. If hyperfine-changing collisions were a significant source of loss in the ground state, we would expect the loss rate to rise at lower fields. Conversely, if the loss is entirely mediated by the formation of collision complexes, it is unlikely to be affected by small changes in the energy of the asymptotic states and the loss rate will be independent of magnetic field.

We have measured loss of molecules at various magnetic fields between 4.6 G and 229.8 G, and over this range the loss rate does not vary outside experimental uncertainties (see Supplementary Note 2). This suggests that loss due to hyperfine-changing collisions is not significant, and is consistent with the sticky collision hypothesis.

Collisions in a mixture of rotational states

We have also measured loss from an incoherent mixture of the spin-stretched states \( N = 0, M_F = +5 \) and \( N = 1, M_F = +6 \). These two states are linked by a dipole-allowed transition, so collisions between them experience an additional resonant dipole-dipole interaction. This is equivalent to the interaction of two space-fixed dipoles \( d = d_0/\sqrt{6} = 0.50 \) D. For s-wave scattering this interaction cancels in first order due to spherical averaging, but for higher partial waves it dies off asymptotically as \( R^{-3} \). Even for s waves, there are strong higher-order effects with leading term proportional to \( R^{-4} \). These terms die off much more slowly than dispersion forces at long range, so may be expected to produce larger loss rates.

We start with a 50:50 mixture of molecules in the two states, at \( T = 1.5(1) \mu \)K, and measure the number re-
mainly in change of the densities \( n_0(t,r) \) and \( n_1(t,r) \), for molecules in \( N = 0 \) and \( N = 1 \) respectively, by the coupled rate equations

\[
\dot{n}_0(t,r) = -k_{20}^{00}n_0(t,r)^2 - \frac{1}{2}k_{21}^{01}n_0(t,r)n_1(t,r), \\
\dot{n}_1(t,r) = -k_{21}^{11}n_1(t,r)^2 - \frac{1}{2}k_{22}^{01}n_0(t,r)n_1(t,r).
\] (3)

We use the values of \( k_{20}^{00} \) and \( k_{21}^{11} \) measured above for molecules in identical rotational states. Fitting yields a value \( k_{22}^{01} = 7.2(9) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) for the loss rate coefficient for collisions between molecules in different rotational states. This is significantly higher than for molecules prepared in a single rotational and hyperfine state and demonstrates a significant increase in the loss rate due to a resonant dipole-dipole interaction.

**DISCUSSION**

We have presented experimental measurements of loss rates for non-reactive RbCs molecules. We have demonstrated that the loss is best described by second-order rate equations. This suggests that the loss is governed by a two-body process and supports the sticky collision hypothesis that the rate-limiting step is formation of long-lived collision complexes [48, 49]. Through investigating the loss from the rotational and hyperfine ground state over a temperature range of 0.85(5) K to 3.3(3) K we have determined the loss probability parameter \( y \) at short range to be less than 0.4. We observe no change in loss rate with varying magnetic field. For rotationally excited states, the loss is up to a factor of 2 faster, probably due to rotational relaxation. For a mixture of rotational states, the loss is much faster, because of resonant dipole interactions.

Our results for the ground state are inconsistent with the universal limit of complete loss at short range. A lower loss probability may be accommodated in the model of Mayle et al. [48, 49] by using an average width smaller than predicted by RRKM theory. This demonstrates a breakdown of ergodicity. A possible interpretation is that complex formation can occur only when the molecules collide at a limited range of relative orientations.

Our value of the loss parameter \( y \) is similar to that seen for reactions of the type (1) in fermionic KRb (\( y \sim 0.4 \) [43, 51]) suggesting that a similar geometric restriction might apply in that case. Takekoshi et al. [3] published results with RbCs at a temperature of 8.7(7) µK, which is significantly higher than the present work. At fields above 90 G, they observed \( k_2 \sim 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \), which is consistent with both our fitted values of \( y \) and \( \delta \) and the universal limit. They also reported an increase in the loss rate by an order of magnitude at lower fields, which they attributed to hyperfine-changing collisions to form lower-energy states. However, as shown in the Supplementary Figure 2, the increased loss rates are larger than the maximum allowed by reflection of the long-range potential at the temperature of the experiment. The only other non-reactive molecule for which collisions have been studied in detail is NaRb; the results were interpreted as consistent with the universal limit [47, 57], but the observed temperature dependence resembles that calculated here for resonant s-wave scattering at lower \( y \), as shown by the orange line in Fig. 3.

In conclusion, our measurements of collisional losses in ultracold RbCs support the sticky collisions hypothesis, but the rates are significantly lower than the universal limit. By examining the temperature dependence, we have seen the first indication of the scattering length for RbCs+RbCs collisions. By preparing an incoherent mixture of ground and first-excited rotational states, we turn on a resonant dipole-dipole interaction which greatly increases the loss rate. Our results indicate that active measures to suppress collisional loss will be needed in experiments with high-density molecular gases, even if the molecules are nonreactive.

**METHODS**

Transfer of molecules to the ground state

We begin our experiments with a sample of weakly-bound RbCs Feshbach molecules [58], confined to a \( \lambda = 1550 \text{ nm ODT} \) at a magnetic field of 181.5 G. We transfer the molecules to a single hyperfine level of the \( \Sigma^+ \) rovibrational ground state via stimulated Raman adiabatic passage (STIRAP) [4] in free-space (i.e. with the trap light off) to avoid a spatially-varying ac Stark shift of the two-photon resonance [59]. The efficiency of the STIRAP is typically 90%, and we can transfer to hyperfine states in \( N = 0 \) with \( M_F = +5 \) or \( M_F = +4 \) depending on the selected laser polarization [60]. Following STIRAP, the molecules are recaptured by turning the trapping light back on. We set the intensity of the trap light before (\( I_{FB} \)) and after (\( I_{GS} \)) STIRAP such that the ground state molecules experience the same trap parameters as they did in the Feshbach state, i.e. \( I_{GS}/I_{FB} = \alpha_{FB}/\alpha_{GS} \) where \( \alpha_{FB}, \alpha_{GS} \) are the polarizabilities of the Feshbach and ground states [61]. The ground-state transfer takes 20 µs and the trap light is off for less than 200 µs in all experiments presented; we detect no significant heating or loss from this modulation of the trap potential.

Detection of molecules

We measure the number of molecules by reversing the association process, dissociating the molecules back to their constituent atoms which are detected via absorption imaging. We therefore only image molecules which occupy the specific hyperfine state accessed through the
STIRAP. We extract the number from each absorption image either by summing pixels in a fixed region of interest or by least squares fitting to a 2D Gaussian function. We find similar numbers using both methods. Results plotted in this work show the numbers found using the pixel summing algorithm.

We produce up to $N_{\text{mol}} = 4000$ ground-state molecules. By varying the hold time between the ground-state molecule recapture and the dissociation for imaging, we record the time evolution of the number of molecules remaining in the dipole trap.

### Measurement of trap frequencies

We measure the trap frequencies experienced by the molecules by observing centre of mass oscillations in the optical potential. We also compare the oscillation frequencies for the molecules to those of atoms in the same potential [61]. For the results shown in Fig. 1, we find $(\omega_x, \omega_y, \omega_z) = 2\pi \times (181(2), 44(1), 178(1))$ Hz where $z$ is in the direction of gravity.

### Measurement of temperatures

The initial temperature of the molecules is measured by ballistic expansion in free space. Due to the small number of molecules, we can only image the cloud over an expansion time of $\sim 2$ ms. For comparison, we also measure the temperature of atoms by the same method in similar trapping conditions. We find good agreement between the temperature of the molecules and that of the atoms. We do not measure the variation of temperature as a function of time during the loss measurement, as the loss of molecules further limits the maximum expansion time available leading to unreliable temperature measurements.

The rate equations (2) we use to model the loss depend on both $N_{\text{mol}}(t)$ and $T(t)$. As described in the main text, we fit $N_{\text{mol}}(t)$ for a fixed initial $T$, allowing the temperature to evolve as a function of time within the constraints of the model. We have also fitted our results assuming the molecules remain at their initial temperature throughout the measurement. In this limit, we find our results are still consistent with a two-body process and for the results in Fig. 1, we extract $k_2 = 3.8(5) \times 10^{-13}$ cm$^3$ s$^{-1}$.

### Optical trapping and varying temperature

To vary the temperature, we adiabatically compress the molecules prior to ground-state transfer. The lowest temperature measurements we perform use the $\lambda = 1550$ nm ODT in which the Feshbach molecules are initially prepared. The trap light is derived from a single mode IPG fibre laser, which is split into two beams with focused waists 80 $\mu$m and 98 $\mu$m crossing at an angle of 27.5°. There is a frequency difference of 100 MHz between the two beams originating from the acousto-optic modulators used to independently control the beam intensities. In this trap we can access temperatures from 0.85(5) $\mu$K to 1.9(1) $\mu$K for geometrically averaged trap frequencies $\bar{\omega}/(2\pi)$ between 70 Hz and 149 Hz. This trap is used for all loss measurements with a temperature of 1.9 $\mu$K or below.

To explore higher temperatures, we transfer the molecules to a different optical potential with $\lambda = 1064.52$ nm. The light is generated by a Coherent Mephisto master oscillator power amplifier, and the trap formed by crossing two beams with focused waists of 64 $\mu$m and 67 $\mu$m (and 160 MHz frequency difference) at an angle of 54°. To transfer the molecules between the two traps, we ramp the powers linearly over 50 ms. In this trap, we performed measurements at temperatures of 2.6(2) $\mu$K and 3.3(3) $\mu$K. The result in Fig. 3 with $T = 2.9(1)$ $\mu$K is performed with a mixed wavelength potential, using one beam of the $\lambda = 1064$ nm trap crossed with one beam of the $\lambda = 1550$ nm trap. This removes the possibility of loss or heating due to the 100/160 MHz beat frequency between the two beams, and allows us to rule out intensity dependent losses from either trap.

### Eliminating other sources of loss

Collisions of ground state molecules with Rb atoms, Cs atoms, or molecules in excited states could also cause loss. Following Feshbach association, we remove the remaining Rb and Cs atoms from the trap via the Stern-Gerlach effect. During the separation the atoms do not experience a trap for over 20 ms, which is sufficient to ensure all atoms have left the region of interest. The STIRAP process is typically 90% efficient, with the ‘lost’ molecules likely being addressed by the pump light and transferred to the $^3\Pi_{\mu}, v = 29, N = 1$ electronically excited state. The lifetime for molecules in this excited state is 16(1) $\mu$s [59], following which the molecules may decay to either $a^3\Sigma^+$ or $X^1\Sigma^+$. We have performed measurements with STIRAP efficiency between 79% and 93% with no measurable change to the loss rate indicating that the molecule fraction which is not transferred to the ground state plays no role in the subsequent loss. This is consistent with similar observations in NaRb [17].

We have observed narrow resonant loss features around 1064.48 nm which are dependent on the laser frequency and intensity. We have investigated the intensity and density dependence of these features and conclude that they result from two-photon excitation of the molecules. All measurements using the 1064 nm trap are performed at a wavelength of 1064.52 nm, sufficiently far from the narrow loss features to remove them as a source of loss.

We also discount other light-scattering losses in our experiments. Loss of molecules due to the absorption of black-body radiation has a rate of $10^{-5}$ s$^{-1}$ for RbCs at
room temperature \cite{02}. For laser light with $\lambda = 1550$ nm, the photon energy is greater than the dissociation energy of the electronic ground state but far below the potential minimum for the $b^3\Pi$ state. Photons of wavelength 1064.52 nm are above the potential minimum of the $b^3\Pi$ state, but transitions to the accessible vibrational levels are strongly suppressed due to small Franck-Condon factors \cite{03}. By performing measurements at these two trapping wavelengths, we demonstrate that the loss we observe is independent of the wavelength of the trap light. Moreover, by using a mixed-wavelength trap, we eliminate the possibility of intensity dependent losses.

**Internal state control and transfer**

Following the ground-state transfer, we pulse on microwaves to perform either a single or a pair of coherent $\pi$-pulses, transferring the molecules to a different rotational and/or hyperfine state. The microwave transfer is performed with the optical trap off, and has unity efficiency \cite{56}. We tune the intensity of the microwaves such that the Rabi frequency is small enough to avoid off-resonant excitation of nearby transitions, while still obtaining a $\pi$ pulse duration of $< 100$ $\mu$s. To read-out the number of molecules in an excited state we must reverse the sequence of $\pi$-pulses to transfer back to the original state used for STIRAP.

Measuring loss in higher rotational states requires a good understanding of the molecular polarizability, and hence the trapping potential observed for each state. The trapping light is linearly polarized parallel to the magnetic field, and in this case the states chosen each have a linear ac Stark shift as a function of laser intensity. This is necessary to avoid possible Landau-Zener type loss associated with avoided crossings between hyperfine states \cite{61}. For each state, we tune the intensity of the optical trap so that the molecules always experience the same trap frequency and depth as they do in the ground state. We do not expect any spontaneous emission from the rotationally excited states as the rate is $\sim 10^{-9}$ s$^{-1}$.

**Preparation of an incoherent mixture**

To generate a 50:50 mixture of molecules in different rotational states, we drive a $\pi/2$-pulse on the transition between $N = 0$, $M_F = +5$ and $N = 1$, $M_F = +6$ in free-space. This puts the molecules into a coherent, equal superposition of the two states. The molecules are recaptured in the $\lambda = 1550$ nm ODT, where the superposition rapidly dephases due to spatial variation in the energy difference between the states \cite{64}. Using Ramsey spectroscopy, we observe no signs of coherence after a 10 $\mu$s hold in the ODT; four orders of magnitude faster than the timescale of the loss. The density matrix which describes the cloud following this dephasing contains only the diagonal elements and thus can be considered a mixed state.

As the two states have different polarizabilities, $\alpha_{N=1}/\alpha_{N=0} \approx 0.9$, we cannot tune the laser intensity to match the trap parameters to those before preparation for both states. We have performed experiments where the trap frequency and depth is matched for either $N = 0$ and $N = 1$, and we measure the same value of $k_\lambda$ in both cases.

**Dispersion coefficients**

Dispersion coefficients $C_6$ arise from the dipole-dipole interaction in second order and may be calculated using perturbation theory. For the interaction of two RbCs molecules, they are dominated by rotational terms involving the permanent molecular dipole moment. The necessary matrix elements can be found in, for example, Ref. \cite{65}. The result for the rotational ground state, $C_{6,\text{rot}} = \mu_6^2/6 B$, is well known. For rotationally excited states, the diagonal part of $C_6$ varies with the projection quantum number $M_N$ and with partial wave $L$. There are additional contributions to $C_6$ from electronic dispersion and induction interactions, which we take from ref. \cite{66}.

We calculate the $C_6$ coefficients using accurate values for the RbCs electric dipole moment $\mu_{\text{elec}} = 1.225$ D \cite{4} and rotational constant $B = 490.173994$ MHz \cite{50}. For the rotational ground state the combination of rotational and electronic contributions gives $C_6 = 141 000 \ E_h a_6^6$. For the rotationally excited state, we find for $L = 0$: $C_6 = 141 000 \ E_h a_6^6$ for $N = 1$, $M_N = 0$; $C_6 = 96 000 \ E_h a_6^6$ for $N = 1$, $M_N = 1$; and $C_6 = 82 000 \ E_h a_6^6$ for $N = 2$, $M_N = 2$.

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I. ACKNOWLEDGEMENTS

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SUPPLEMENTARY NOTE 1: DERIVATION OF RATE EQUATIONS (2)

We model the rate of change of density $\dot{n}(r,t) = -k_\gamma n(r,t)$. Here the power of the density $\gamma = 1, 2, 3$ corresponds to losses governed by one-, two-, and three-body processes respectively, and $k_\gamma$ is the collision rate coefficient for the $\gamma$-body loss. For a thermal ensemble trapped in a harmonic trap the density is given by

$$n(r,t) = \frac{N_{\text{mol}}(t) \omega_x \omega_y \omega_z m^{3/2}}{(2\pi k_B T(t))^{3/2}} e^{-\frac{m[\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2]}{2k_B T(t)}}.$$

Here, $N_{\text{mol}}(t)$ is the number of molecules remaining, $T(t)$ is the temperature of the remaining distribution, $m$ is the mass of the molecule, $k_B$ is the Boltzmann constant, and $\omega_x$, $\omega_y$, $\omega_z$ are the trapping frequencies in the $x$, $y$, $z$ directions respectively. The rate of change of the number of molecules can be then obtained by integrating $\dot{n}(r,t)$,

$$\dot{N}_{\text{mol}}(t) = \int \dot{n}(r,t) d^3r = -k_\gamma C(\gamma-1) \left( \frac{N_{\text{mol}}(t)^\gamma}{\gamma^{3/2} T(t)^{3/2}(\gamma-1)} \right),$$

where $C = (m\bar{\omega}^2 / 2\pi k_B)^{3/2}$ and $\bar{\omega} = \sqrt[3]{\omega_x \omega_y \omega_z}$ is the geometric mean of the trapping frequencies.

The temperature of the remaining molecules will change as a function of time. This is due to molecules being preferentially lost from the centre of the trap where the density is highest. The probability that loss occurs at a given location and time can be calculated as $p_{\text{loss}}(r) = \frac{n(r,t)^{\gamma-1}}{\int n(r,t)^{\gamma-1} d^3r}$. The average energy of the colliding molecules can therefore be calculated as,

$$E_{\text{coll}} = \int p_{\text{loss}}(r) \frac{m}{2} (\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) \, dx \, dy \, dz = \frac{3k_B T(1+\gamma)}{2\gamma}.$$

Here we have assumed that the molecules remain in thermal equilibrium at all times and that $k_\gamma$ is independent of the velocities of the molecules undergoing collisions. The total energy at time $t$ is $3k_B T(t)N_{\text{mol}}(t)$. If $\Delta N_{\text{mol}} = N_{\text{mol}}(t) - N_{\text{mol}}(t + \delta t)$ molecules are lost in time $\delta t$ and the temperature changes to $T(t + \delta t)$, the total energy at time $t + \delta t$ is, $3k_B T(t + \delta t)[N_{\text{mol}}(t) - \Delta N_{\text{mol}}] = 3k_B T(t)N_{\text{mol}}(t) - \Delta N_{\text{mol}} E_{\text{coll}}$. For small $\delta t$ this gives a rate equation for the temperature,

$$\dot{T}(t) = \frac{\dot{N}_{\text{mol}}(t) (3k_B T(t) - E_{\text{coll}})}{N_{\text{mol}}(t)} = k_\gamma C(\gamma-1) \left( \frac{\gamma - 1}{2\gamma} \right) \left( \frac{N_{\text{mol}}(t)^{\gamma-1}}{\gamma^{3/2} T(t)^{3(\gamma-5)/2}} \right).$$

(7)
SUPPLEMENTARY NOTE 2: EXPERIMENTS AT DIFFERENT MAGNETIC FIELDS

As discussed in the main text, to investigate loss of molecules at a range of magnetic fields, we transfer the molecules to the ground state with $B = 181.5$ G. We then ramp the magnetic field to the desired value linearly over 50 ms. After a variable hold time, $B$ is ramped back to 181.5 G over a further 50 ms before dissociation and imaging. The measured loss rates for a range of magnetic fields between 4.6 G and 229.8 G are shown in Supplementary Fig. 1.

![Supplementary Figure 1: Dependence of loss rate on magnetic field. Upper panel: Hyperfine Zeeman structure of RbCs in the rotational ground state. Molecules occupy the spin-stretched state $N = 0, M_F = +5$ highlighted. Lower panel: Measured two-body loss rate coefficient as a function of magnetic field for molecules with initial temperature $T = 1.5 \mu$K. We observe no variation in the loss rate even when the occupied hyperfine state is no longer the lowest energy. The horizontal red line indicates the average loss rate coefficient of 4.4(1) cm$^3$ s$^{-1}$ across all the results shown.](image-url)
### SUPPLEMENTARY NOTE 3: NUMERICAL VALUES FOR RESULTS SHOWN IN FIG. (4)

Supplementary Table 1: Loss rates measured in a range of rotational and hyperfine states. Molecules are prepared in a state \((N, M_F)\) with \(T = 1.5 \, \mu K\) and \(B = 181.5 \, G\). The energy of each state \(E/h\) is given with respect to \((0, +5)\) state, which at this magnetic field has the lowest energy. Asterisks indicate measurements where the state is populated directly with STIRAP.

| \((N, M_F)\) | \(E/h\) (kHz) | \(k_{2}^{\text{univ}}(0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}\) | \(k_{2}^{\text{univ}}(1.5 \, \mu K) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}\) | \(k_{2}^{\text{exp.}} \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}\) |
|--------------|----------------|------------------|------------------|------------------|
| \((0, +5)*\)  | 0              | 17.9             | 9.9              | 4.8(6)           |
| \((0, +5)*\)  | 0              | 17.9             | 9.9              | 4.5(8)           |
| \((0, +4)\)   | 58             | 17.9             | 9.9              | 6.3(7)           |
| \((0, +4)*\)  | 201            | 17.9             | 9.9              | 5.8(5)           |
| \((0, +4)\)   | 201            | 17.9             | 9.9              | 6.4(7)           |
| \((1, +5)\)   | 980,231        | 17.9             | 9.9              | 6.4(9)           |
| \((1, +6)\)   | 980,385        | 16.3             | 9.4              | 6.2(8)           |
| \((2, +7)\)   | 2,941,090      | 15.8             | 9.1              | 9(1)             |
Supplementary Figure 2: Contour plot of thermally averaged loss rate coefficients $k_2$ for RbCs from the single-channel model at 8.7 µK. This temperature corresponds to measurements of loss reported in [3]. In this work, Takekoshi et al. observed fast loss of up to $10^{-9}$ cm$^3$ s$^{-1}$ in magnetic fields below $\sim 90$ G, which was attributed hyperfine-changing collisions. However, loss rates this high are larger than the maximum allowed by reflection off the long-range potential at the temperature of the experiment.