Reaction kinetics of ultracold molecule-molecule collisions

Daniel K. Hoffmann,1 Thomas Paintner,1 Wolfgang Limmer,1
Dmitry S. Petrov,2 and Johannes Hecker Denschlag1

1Institut für Quantenmaterie and Center for Integrated Quantum Science and Technology (IQST),
Universität Ulm, D-89069 Ulm, Germany
2LPTMS, CNRS, Univ. Paris Sud, Université Paris-Saclay, 91405 Orsay, France

Studying chemical reactions on a state-to-state level tests and improves our fundamental understanding of chemical processes. For such investigations it is convenient to make use of ultracold atomic and molecular reactants as they can be prepared in well defined internal and external quantum states. In general, even cold reactions have many possible final product states and reaction channels are therefore hard to track individually. In special cases, however, only a single reaction channel is essentially participating, as observed e.g. in the recombination of two atoms forming a Feshbach molecule or in atom-Feshbach molecule exchange reactions. Here, we investigate a single-channel reaction of two Li2-Feshbach molecules where one of the molecules dissociates into two atoms \(2\text{AB} \rightarrow \text{AB} + \text{A} + \text{B} \). The process is a prototype for a class of four-body collisions where two reactants produce three product particles. We measure the collisional dissociation rate constant of this process as a function of collision energy/temperature and scattering length. We confirm an Arrhenius-law dependence on the collision energy, an \(a^4\) power-law dependence on the scattering length \(a\) and determine a universal four body reaction constant.
We carry out the experiments with an ultracold, mixed gas of $\text{Li}_2$ Feshbach molecules and unbound Li atoms for which the reaction dynamics is governed by a detailed balance. By measuring the particle numbers for different settings in and out of equilibrium we determine the reaction rate constants for collisional dissociation and association of a $\text{Li}_2$ molecule. We find that the dissociation rate constant strongly depends on the temperature and the scattering length, in agreement with theoretical predictions.

The initial atomic and molecular sample is prepared from an ultracold gas of $N_{\text{tot}} = 2.6 \times 10^5$ fermionic $^6\text{Li}$ atoms which consists of a balanced mixture of the two lowest hyperfine states $|m_F = \pm 1/2 \rangle$ of the electronic ground state. In the vicinity of the Feshbach resonance at $B_0 = 832.2 \text{G}$ (see ref.\textsuperscript{22}) exothermic three-body recombination can convert pairs of $|-1/2\rangle, |+1/2\rangle$ atoms into weakly-bound Feshbach molecules, each of which is in the same internal quantum state. The process is reversible and a Feshbach molecule can dissociate again into the unbound $|-1/2\rangle, |+1/2\rangle$ atoms via an inelastic, endothermic collision with another molecule or atom. At thermal equilibrium balance of the back and forth reactions is established. This balance is a function of the particle densities, temperature, molecular binding energy, and scattering length, all of which can be controlled in our setup via confinement, evaporative cooling, and by choosing a magnetic offset field $B < B_0$. Our trap is a combination of a magnetic trap and an optical dipole trap and is cigar shaped. The trap has a depth of $U_0 = 21 \mu\text{K} \times k_B$, corresponding to a radial (axial) trapping frequency of $\omega_r = 2\pi \times 0.99\text{kHz}$ ($\omega_{ax} = 2\pi \times 21\text{Hz}$), respectively. We use evaporative cooling to set the temperature to approximately 1.2 to 1.3 $\mu$K. At this temperature 80% to 90% of all atoms are bound in Feshbach molecules within the $B$-field range of 705 G to 723 G of our experiments, corresponding to a binding energy $E_b$ between 6 and 10 $\mu\text{K} \times k_B$ (see Methods). We note that at these settings where $T \geq T_F$ ($T_F$ is the Fermi temperature) and $E_b > k_BT_F$, quantum degeneracy only plays a negligible role for the reaction kinetics.

In our first experiment we suddenly raise the temperature of the gas using an excitation pulse of parametric heating. This shifts the gas out of thermal equilibrium and the gas responds by collisionally dissociating a part of its molecules, (see fig. [1]b). For this, we modulate the dipole trap depth (see fig. [1]b) with frequency $\omega_{\text{heat}} \approx 1.7\omega_r$ and amplitude $\Delta U = 0.21U_0$ during a period $t_p = 20\text{ms}$. After the excitation atoms and dimers thermalize on a time scale of a few milliseconds via elastic collisions, whereas the chemical equilibrium requires a much longer time of 150 ms.

To investigate these dynamics we measure how the number of molecules $N_M$ and the number of unbound atoms $N_A$ change as a function of time. We measure $N_A$ by using standard absorption
Figure 1. **Molecule dissociation dynamics.** a, Detailed balance of collisional dissociation and association of dimers. b, A parametric heating pulse triggers the reaction dynamics. c, As part of the detection scheme, the Feshbach molecules which have a large admixture of the X$^1\Sigma_g^+$, $v = 38$ state are optically pumped to undetected atomic or molecular states via the intermediate level $A^1\Sigma_u^+$, $v' = 68$. d, Measurement of dissociation dynamics at 709 G. Lower part: Circle (triangle) symbols show the number of unbound atoms $N_A$ ($\tilde{N}_A$) for variable holding time $t$ with (without) initial parametric heating pulse. Upper part: Diamond (square) symbols show the total particle number $N_{tot}$ ($\tilde{N}_{tot}$) with (without) parametric heating pulse.

imaging. However, prior to the imaging we first remove all Feshbach molecules from the gas. For this, a resonant laser pulse transfers the molecules to an electronically excited molecular state $A^1\Sigma_u^+$, $v' = 68$ which subsequently decays with in a few ns to undetected atomic or molecular states (see fig. 1c), see Methods. The laser pulse has a duration of 0.5 ms which is short compared to the reaction dynamics. In order to determine $N_M$ we measure in a second run the total number of atoms $N_{tot} = 2N_M + N_A$, whether they are bound or unbound, and subtract $N_A$. For this we use again absorption imaging. The Feshbach molecules are so weakly bound that the imaging laser resonantly dissociates them quickly into two cold atoms which are subsequently detected via absorption imaging.

Figure 1d shows the measurements of $N_A$ and $N_{tot}$ as a function of holding time after the heating pulse. While the total number of atoms $N_{tot}$ is essentially constant apart from some slow background losses, the atom number $N_A$ exhibits a 30% increase in about 100 ms which is the dissociation response of Li$_2$ molecules to the thermal pulse. Besides this, $N_A$ also exhibits a slow, steady increase which we attribute to a background heating of the gas, e.g. due to spontaneous photon scattering of the dipole trap light (see Supplementary Information). As shown by $\tilde{N}_A$ in
fig. 1d) this background heating is also present in the absence of the initial heating pulse. Similarly, the slow decay of $N_{tot}$ is also present without the heating pulse (see $\tilde{N}_{tot}$ in fig. 1d). It can be completely explained by inelastic collisions between molecules as previously investigated in ref \(^2\text{6}\).

In principle, collisional dissociation in our experiment can be driven either by atom-molecule collisions or by molecule-molecule collisions. We only consider molecule-molecule dissociation since its rate is about two orders of magnitude larger in our experiments than for atom-molecule dissociation with its known rate constant of \(^2\text{7}\) $C_1 \approx 10^{-13}$ cm\(^3\)/s and given the fact that the mean density of atoms is a factor of ten smaller than for the dimers. In a simple physical picture, the suppression of the atom-dimer dissociation is due to the Pauli principle acting on the outgoing channel, which involves two identical fermionic atoms \(^2\text{8,29}\). In the molecule-molecule collisional dissociation, the molecules can either dissociate into four unbound atoms, $2AB \Rightarrow 2A + 2B$, or into two unbound atoms, $2AB \Rightarrow AB + A + B$. However, since in our experiments the molecular binding energy $E_b$ is typically by a factor of 5 larger than the thermal energy $k_B T$, the dissociation into four atoms comes at an additional sizeable energy cost and is therefore comparatively suppressed by an Arrhenius factor of \(\exp(-E_b/k_B T) \approx 7 \times 10^{-3}\), see also \(^2\text{7}\). Therefore, to first order, we only need to consider dissociation into two atoms. The evolution of the density $n_A$ of unbound atoms is then given by the rate equation,

$$\dot{n}_A = 2C_2 n_M^2 - R_2 n_A^2 n_M/2$$

(1)

Here, $n_M$ is the molecule density and $C_2$ ($R_2$) are the rate constants of molecule dissociation (association). A spatial integration of eq. (1) gives the rate equation for the number of unbound atoms,

$$\dot{N}_A = \left(4\pi^{3/2}\right)^{-1} \frac{C_2}{\sigma_r^2 \sigma_{ax}^2} N_M^2 - 2^{-7} (2\pi^2)^{-3/2} \frac{R_2}{\sigma_r^4 \sigma_{ax}^4} N_A^2 N_M$$

(2)

where we assume a Boltzmann distribution in a harmonic trap. Here, $\sigma_r$ ($\sigma_{ax}$) denote the radial (axial) cloud width of the molecular gas and $m$ is the mass of $^6$Li. Furthermore, in eq. (2) we have used the fact that the cloud size for the unbound atoms is $\sigma_{r(ax)} = \sqrt{2}\sigma_{r(ax)}$. By fitting eq. (2) to the data of fig. 1d we can determine the rate coefficients to be $C_2 = (2.0 \pm 0.6) \times 10^{-12}$ cm\(^3\)/s and $R_2 = (4.1 \pm 1.2) \times 10^{-22}$ cm\(^6\)/s. For the fit we use the measured widths $\sigma_{r(ax)}$ which turn out to be fairly constant during the holding time $t$ (a more detailed discussion will be given below).

Next, we investigate how the reaction rates depend on temperature. For this, it is convenient to study the atom molecule system in a state of near equilibrium, where $\dot{N}_A \approx 0$, i.e. $\dot{N}_A$ is much
Figure 2. Temperature dependence of the equilibrium state and temperature evolution. a, The ratio $C_2/R_2$ (circles) is plotted as a function of temperature $T$ at $B = 723\text{G}$. The errorbars denote the 1σ uncertainty in the thermometry. The continuous line is a calculation without any free parameters (see text). b, Measured evolution of the axial cloud size $\sigma_{ax}$ (green circles) at $B = 705\text{G}$ after injecting a heat pulse during $-20\text{ms} < t < 0\text{ms}$ (vertical dashed lines). The heat pulse abruptly increases the temperature $T$ and size $\sigma_{ax} \propto \sqrt{T}$. In addition it excites small collective breathing mode oscillations, see red line as a guide to the eye. The red dots mark the evolution of $\sigma_{ax}$ when averaged over one oscillation period. This evolution is well described by a model calculation (blue line) as described in the Supplementary Material. The temperature scale applies to the non-oscillatory part of the data.

smaller than the individual collisional dissociation/association rates of eq. 2. We can then set $C_2/R_2 = 2^{-5}(2\pi)^{-3/2}\frac{1}{\sigma_{ax}^2 N_A N_M}$. Thus, a change in the ratio $C_2/R_2$ due to a variation in temperature, can be experimentally observed in terms of a change of particles numbers and widths. Figure 2a shows such measurements at $B = 723\text{G}$ ($N_A$ was always at least a factor of ten smaller than the collisional dissociation/association rates). Within the small temperature range between 1 and $3\mu\text{K}$, the rate constant ratio $\frac{C_2}{R_2}$ increases by more than two orders of magnitude. This result can be compared to a prediction based on statistical mechanics$^{27}$,

$$\frac{C_2}{R_2} = h^{-3}(\pi m k_B T)^{3/2} e^{-E_b/k_B T}$$

(3)

which is shown in Fig. 2a as a continuous line with no adjustable parameters. The agreement between experiment and theory is quite good. The strong increase of $\frac{C_2}{R_2}$ with temperature is dominated by the Arrhenius law exponential $e^{-E_b/k_B T}$ which comes into play for the endothermic dissociation ($C_2$) but is absent for the exothermic recombination process ($R_2$).

The strong temperature dependence of the rate constants potentially has a strong influence on
the reaction dynamics of our atom/molecule system, as the chemical reactions change the temperature of the gas. To quantify this influence, we take a closer look at the temperature evolution in our experiment by tracking the cloud size $\sigma_{\text{ax}} \propto \sqrt{T}$, see fig. 2b. Initially the system is in thermal equilibrium and the molecular cloud has an axial cloud size of about $\sigma_{\text{ax}} = 230 \mu$m which corresponds to a temperature of $T \approx 1.3 \mu$K. The heating pulse, which starts at $t = -20$ ms and ends at $t = 0$, deposits thermal energy in the system. Due to the fast elastic collisions of dimers and atoms the thermal energy deposition results in a fast increase of the cloud size of about 6% which corresponds to a temperature increase of $\Delta T \approx 0.15 \mu$K. In addition, the modulation of the dipole trap during the heating pulse excites unwanted breathing mode oscillations in the cloud with a small amplitude of two percent. The mean cloud size which is obtained by averaging over one oscillation (red circles in fig. 2b) is almost constant within the first 150 ms after the heating pulse. This might be at first surprising since one might expect the endothermic dissociation to considerably lower the temperature again. However, since the initial atom number is quite small, only a small amount of molecules need to break up to significantly increase the recombination rate $\propto N_A^2$ and thus to reach a new balance. Therefore only a small amount of the injected heat is consumed for the dissociation, corresponding to a small amount of cooling. Moreover, this residual cooling is almost canceled by the background heating. As a consequence the remaining temperature variation is less than 1%. For later times, $t > 150$ ms, when the reaction triggered by the heating pulse has already stopped, the background heating leads to monotonically increasing mean cloud size. From our results in fig. 2a we conclude that a temperature variation of 1% leads to $C_2/R_2$ variations of at most a few percent, which is negligible with respect to our current measurement accuracy.

In view of these complex dynamics we have set up a system of coupled differential equations that describe in a more complete fashion the various reaction/loss processes at varying temperatures (see Supplementary Material). The solid curve in fig. 2b) is a result of these calculations which in general show very good agreement with our measurements.

Finally, we investigate the influence of the interaction strength between the particles on the reaction dynamics. For this, we tune the scattering lengths with the help of the magnetic $B$-field. We note that the dimer-dimer scattering length $a_{dd}$ is given by $a_{dd} = 0.6a$, where $a$ is the scattering length for atom-atom collisions. Figure 3a shows three measurements for $a = (1760, 1920, 2000) a_0$. For technical reasons, we start with three different $N_A$ at $t = 0$. However, this has negligible influence on the dynamics of the dissociation, which we have checked with a
Figure 3. **Dependence of the reaction rate constants on the scattering length.**

**a,** Reaction dynamics for three scattering lengths of \( a = (1760, 1920, 2000) a_0 \) (green squares, red diamonds and blue circles), corresponding to the magnetic fields \( B = (705, 711, 714) G \), respectively. The continuous lines are fits based on eq. 2 from which \( R_2 \) and \( C_2 \) can be extracted.

**b,** The measured association rate constant \( R_2 \) as a function of \( a \) (red diamonds). \( R_2 \) roughly follows the universal relation \( R_2 = C \hbar a^4 / m \), with \( C = 470 \) obtained from a fit to the data (red continuous line). The majority of the data lies in a band between the curves with \( C = 370 \) and 570 (grey lines).

**c,** The dissociation rate constant \( C_2 \) (red diamonds) as a function of \( a \). The temperatures between the individual measurements varied by about 15%. To compensate the influence of the temperature we use eq. 4 to rescale \( C_2 \) to values corresponding to \( T = 1.5 \mu K \) (blue circles). The error bars correspond to temperature uncertainties and the 95% confidence bounds determined by fits as in **a.** The blue continuous line is the theoretical prediction of eq. 4 for a universal constant of \( C = 470 \).

**Figure 3.**

- **Dependence of the reaction rate constants on the scattering length.**
  - **a,** Reaction dynamics for three scattering lengths of \( a = (1760, 1920, 2000) a_0 \) (green squares, red diamonds and blue circles), corresponding to the magnetic fields \( B = (705, 711, 714) G \), respectively. The continuous lines are fits based on eq. 2 from which \( R_2 \) and \( C_2 \) can be extracted.
  - **b,** The measured association rate constant \( R_2 \) as a function of \( a \) (red diamonds). \( R_2 \) roughly follows the universal relation \( R_2 = C \hbar a^4 / m \), with \( C = 470 \) obtained from a fit to the data (red continuous line). The majority of the data lies in a band between the curves with \( C = 370 \) and 570 (grey lines).
  - **c,** The dissociation rate constant \( C_2 \) (red diamonds) as a function of \( a \). The temperatures between the individual measurements varied by about 15%. To compensate the influence of the temperature we use eq. 4 to rescale \( C_2 \) to values corresponding to \( T = 1.5 \mu K \) (blue circles). The error bars correspond to temperature uncertainties and the 95% confidence bounds determined by fits as in **a.** The blue continuous line is the theoretical prediction of eq. 4 for a universal constant of \( C = 470 \).

Numerical calculation. Already from the data shown in fig. 3a it is obvious that the dissociation rates strongly increase with the scattering length. From fits to these and additional measurements we extract \( R_2(a) \) and \( C_2(a) \) for various scattering lengths and plot the results on a double logarithmic scale in fig. 3b, c (red diamonds).

The association (three-body recombination) process characterized by the rate constant \( R_2 \) has been extensively discussed for various Efimovian systems\(^{31–33}\), where it depends on the three-body parameter, and for non-Efimovian Fermi-Fermi mixtures, where it is suppressed in the low-energy limit\(^{28,29}\). By contrast, here we are dealing with a non-Efimovian system of three distinguishable particles, for which a simple dimensional analysis\(^{34}\) predicts the low-energy threshold law \( R_2 = C \hbar a^4 / m \), where \( C \) is a universal constant. In fig. 3b this \( a^4 \) scaling behavior is plotted for \( C = 470 \), obtained from a fit to our data. Our results show quite good agreement with the expected power law dependence within the error bars. Figure 3c shows \( C_2 \) for various \( a \) (red diamonds). These data are still raw in the sense that each measurement is taken at a slightly different temperature which increases with the scattering length (see Supplementary Material for details). In order to
compensate this temperature change we use eq. [3] to rescale the measured $C_2$ rate constants to values corresponding to a constant temperature $T = 1.5 \, \mu\text{K}$ (see blue circles in fig. [3b]). The resulting rate constant $C_2$ increases by more than one order of magnitude in the tuning range and agrees reasonably with the theoretical prediction (without any free parameter),

$$C_2 = C \frac{(\pi mk_B)^{1/2}}{2\hbar^2} k_B T^{3/2} a^4 e^{-E_b(a)/k_BT},$$

which is obtained by inserting $R_2 = C h a^4/m$ into eq. [3] and using again $C = 470$. As far as we know there is no direct theoretical prediction for this number. D’Incao and co-workers calculated dimer-dimer elastic and inelastic scattering properties in a wide range of collision energies. For the energy interval relevant here, these calculations indicate $30 \lesssim C \lesssim 100$ which is also consistent with our own numerical estimates based on [30,36]. The large discrepancy between the theoretical and experimental value needs to be investigated in future studies.

In conclusion, we have investigated the collisional dissociation of ultracold molecules in a single reaction channel which is characterized by the precisely defined quantum states of the involved atoms and molecules. Using a heating pulse we shift an atom/molecule mixture which is initially in detailed balance out of equilibrium and measure the evolution of the system until it reaches a new equilibrium. This allows us to determine reaction rate constants, in particular for the collisional dissociation of two molecules. Furthermore, we find a strong temperature dependence of this rate which is consistent with the well known Arrhenius equation. In addition, we find agreement of the association (dissociation) rate constant with a scaling behavior of $a^4 \left(a^4 e^{-E_b/k_BT}\right)$, respectively. From our data we estimate the universal constant $C \approx 470$, which is in discrepancy with the theoretical prediction. For the future, we plan to extend the current work to study the dynamics of chemical reactions in a regime, where Fermi and Bose statistics play an important role.
METHODS

Preparation of the atomic and molecular quantum gas

To prepare our sample of ultracold atoms and molecules, we initially trap $10^9$ $^6$Li atoms in a magneto-optical trap, where the atoms are cooled to a temperature of 700 µK. The particles are transferred to an optical dipole trap of a focused 1070nm laser beam with an efficiency of 1%. To generate a balanced distribution (50%/50%) of atoms in the $|m_F = \pm 1/2\rangle$ spin states we apply a resonant 100ms radio frequency pulse. Initially the optical trap has a depth of $4 \text{mK} \times k_B$ and is subsequently ramped down within 6s to $1.3 \text{µK} \times k_B$ to perform forced evaporative cooling. This is carried out at a magnetic field of 780G and during this process Feshbach molecules form via three-body recombination. To suppress particle loss in the experiments and to assure harmonicity of the trapping potential, the trap depth is ramped up again to $U_0 = 21 \text{µK} \times k_B$ after evaporation. We then ramp the $B$-field in a linear and adiabatic fashion to the specific value at which the experiment will be carried out, within the range of 705G to 723G. After a holding time of 100ms the gas has a temperature of approximately 1.2 to 1.3 µK and is in chemical equilibrium, with 80% to 90% of all atoms being bound in Feshbach molecules. The binding energy of the molecules can be determined from $E_b = \frac{\hbar^2}{m(a-\bar{a})^2} \left( 1 + 2.92 \frac{\bar{a}}{a-\bar{a}} - 0.95 \frac{\bar{a}^2}{(a-\bar{a})^2} \right)$ using $\bar{a} = 29.9 a_0$, which yields values between 6 and 10 µK × $k_B$ in our B-field range. The scattering length $a$ as a function of the B-field is taken from ref.22. It can be approximated with $a = a_{bg} \left( 1 - \frac{\Delta B}{B - B_0} \right)$, where $\Delta B = -263.3 \text{G}$ is the width of the resonance and $a_{bg} = -1582 a_0$ is the background scattering length.

Removing of Feshbach molecules

To optically pump the Feshbach molecules into undetected states, we use a 673nm laser with a peak intensity of $I_0 = 500 \text{mW/cm}^2$ which excites all Feshbach molecules to the $A^1\Sigma_u^+, v'=68$ state (see fig. 1c) within 500µs. The excited molecular state decays within a few ns either into two unbound atoms which quickly leave the trap or into deeply bound Li$_2$ molecules which are invisible for our detection.
Acknowledgements

The authors thank C. Chin for fruitful discussions, W. Schoch and B. Deissler for their work in the early stages of the experiment, and J. D’Incao for providing us with the data of ref. This work was supported by the German research foundation Deutsche Forschungsgemeinschaft (DFG) within SFB/TRR21 and by the Baden-Württemberg Foundation and the Center for Integrated Quantum Science and Technology (IQST), and by the European Research Council (FR7/2007-2013 Grant Agreement No. 341197).

1 Krems, R. et al., Cold controlled chemistry. Phys. Chem. Chem. Phys. 10, 4079–4092 (2008).
2 Carr, L., DeMille, D., Krems,R., and Ye, J., Cold and ultracold molecules: science, technology and applications. New J. Phys. 11, 055049 (2009).
3 Quéméner, G., and Julienne, P., Ultracold Molecules under Control! Chem. Rev. 112, 4949–5011 (2012).
4 Richter, F. et al. Ultracold chemistry and its reaction kinetics. New J. Phys. 17, 055005 (2015).
5 Mukaiyama, T., Abo-Shaeer, J., Xu, K., Chin, J., and Ketterle, W., Dissociation and Decay of Ultracold Sodium Molecules. Phys. Rev. Lett. 92, 180402 (2004).
6 Zahzam, N., Vogt, T., Mudrich, M., Comparat, D., and Pillet, P., Atom-Molecule Collisions in an Optically Trapped Gas. Phys. Rev. Lett. 96, 023202 (2006).
7 Staanum, P., Kraft, S., Lange, J., Wester, R., and Weidemüller, M., Experimental Investigation of Ultracold Atom-Molecule Collisions. Phys. Rev. Lett. 96, 023201 (2006).
8 Syassen, N., Volz, T., Teichmann, S., Dürr, S., and Rempe, G., Collisional decay of $^{87}$Rb Feshbach molecules at 1005.8 G. Phys. Rev. A 74, 062706 (2006).
9 Zirbel, J. et al., Collisional Stability of Fermionic Feshbach Molecules. Phys. Rev. Lett. 100, 143201 (2008).
10 Ferlaino, F. et al., Collisions between Tunable Halo Dimers: Exploring an Elementary Four-Body Process with Identical Bosons. Phys. Rev. Lett. 101, 023201 (2008).
11 Ospelkaus, S. et al., Quantum-State Controlled Chemical Reactions of Ultracold Potassium-Rubidium Molecules. Science 327, 853–857 (2010).
12 Ni, K.-K. et al., Dipolar collisions of polar molecules in the quantum regime. Nature 464, 1324–1328 (2010).
Miranda, M. et al., Controlling the quantum stereodynamics of ultracold bimolecular reactions. Nat. Phys. 7, 502–507 (2011).

Wang, T. et al. Deviation from Universality in Collisions of Ultracold $^6$Li$_2$ Molecules. Phys. Rev. Lett. 110, 173203 (2013).

Drews, B., Deiß, M., Jachymski, K., Idziaszek, Z., and Hecker Denschlag, J. Inelastic collisions of ultracold triplet Rb$_2$ molecules in the rovibrational ground state. Nat. Commun. 8, 14854 (2017).

Wolf, J. et al. State-to-state chemistry for three-body recombination in an ultracold rubidium gas. Science 358, 921-924 (2017).

Jochim, S. et al. Pure Gas of Optically Trapped Molecules Created from Fermionic Atoms. Phys. Rev. Lett. 91, 240402 (2003).

Cubizolles, J., Bourdel, T., Kokkelmans, S., Shlyapnikov, G., and Salomon, C. Production of Long-Lived Ultracold Li$_2$ Molecules from a Fermi Gas. Phys. Rev. Lett. 91, 240401 (2003).

Regal, C., Greiner, M., and Jin, D. Lifetime of Molecule-Atom Mixtures near a Feshbach Resonance in $^{40}$K. Phys. Rev. Lett. 92, 083201 (2004).

Rui, J. et al. Controlled state-to-state atom-exchange reaction in an ultracold atom-dimer mixture. Nat. Phys. 13, 699–703 (2017).

Knoop, S. et al. Magnetically controlled exchange process in an ultracold atom–dimer mixture. Phys. Rev. Lett. 104, 053201 (2010).

Zürn, G. et al. Precise Characterization of $^6$Li Feshbach Resonances Using Trap-Sideband-Resolved RF Spectroscopy of Weakly Bound Molecules. Phys. Rev. Lett. 110, 135301 (2013).

Partridge, G., Strecker, K., Kamar, R., Jack, M., and Hulet, R. Molecular Probe of Pairing in the BEC-BCS Crossover. Phys. Rev. Lett. 95, 020404, (2005).

Paintner, T. et al., Temperature dependence of the pairing fraction in the BEC-BCS crossover. arXiv 1803.10598.

Ketterle, W. and Zwierlein, M., in Ultra-cold Fermi Gases, International School of Physics “Enrico Fermi”, Vol. Course CLXIV, edited by Inguscio, M., Ketterle, W., and Salomon, C. (IOS Press, 2008).

Bourdel, T. et al., Experimental Study of the BEC-BCS Crossover Region in Lithium 6. Phys. Rev. Lett. 93, 050401 (2004).

Chin, C., and Grimm, R. Thermal equilibrium and efficient evaporation of an ultracold atom-molecule mixture Phys. Rev. A 69, 033612 (2004).
28 Petrov, D. S. Three-body problem in Fermi gases with short-range interparticle interaction *Phys. Rev. A* **67**, 010703(R) (2003).

29 D’Incao, J.P. and Esry, B. D. Scattering Length Scaling Laws for Ultracold Three-Body Collisions *Phys. Rev. Lett.* **94**, 213201 (2005).

30 Petrov, D., Salomon, C., and Shlyapnikov, G. Weakly Bound Dimers of Fermionic Atoms. *Phys. Rev. Lett.* **93**, 090404 (2004).

31 Ferlaino, F. et al. Efimov resonances in ultracold quantum gases. *Few-Body Sys.* **51**, 113–133 (2011).

32 Pires, R. et al. Observation of Efimov Resonances in a Mixture with Extreme Mass Imbalance. *Phys. Rev. Lett.* **112**, 250404 (2014).

33 Tung, S.-K. et al. Observation of geometric scaling of Efimov states in a Fermi-Bose Li-Cs mixture. *Phys. Rev. Lett.* **113**, 240402 (2014).

34 Fedichev, P., Reynolds, M., and Shlyapnikov, G. Three-Body Recombination of Ultracold Atoms to a Weakly Bound s Level. *Phys. Rev. Lett.* **77**, 2921–2924 (1996).

35 D’Incao, J. P., Rittenhouse, S. T., Mehta, N., and Greene, C. Dimer-dimer collisions at finite energies in two-component Fermi gases. *Phys. Rev. A* **79**, 030501 (2009).

36 Petrov, D. S., Salomon, C. and Shlyapnikov, G. V. Scattering properties of weakly bound dimers of fermionic atoms. *Phys. Rev. A* **71**, 012708 (2005).

37 Julienne, P. and Hutson, J. Contrasting the wide Feshbach resonances in $^6$Li and $^7$Li. *Phys. Rev. A* **89**, 052715 (2014).
SUPPLEMENTARY INFORMATION

Modeling of the reaction dynamics

We perform model calculations to describe in more detail the measured dynamics of the atom/molecule system, triggered by the initial heat pulse. For this, we integrate the following coupled system of rate equations for the atom number $N_A$, the molecule number $N_M$ and the temperature $T$,

\begin{align}
\dot{N}_A &= C_2 a_1 \frac{N_M^2}{\sigma_r^2 \sigma_{ax}} - R_2 a_2 \frac{N_M N_A^2}{\sigma_r^4 \sigma_{ax}^2} \\
\dot{N}_M &= -\frac{\dot{N}_A}{2} - C_{DD} a_1 \frac{N_M^2}{2 \sigma_r^2 \sigma_{ax}} \\
\dot{T} &= -\frac{E_b}{6 k_B (N_A + N_M)} \dot{N}_A + C_H
\end{align}

where $a_1 = (4\pi^{3/2})^{-1}$ and $a_2 = 2^{-7}(2\pi^2)^{-3/2}$ are numerical constants. Equation (1) is identical to eq. (2) in the main text. The first term in eq. (2) corresponds to the conversion between molecules and unbound atoms, while the second term accounts for molecule losses in inelastic dimer-dimer collisions with rate constant of $C_{DD} = 2.3 \times 10^{-13}$ cm$^3$/s, which is extracted from the previous measurement of ref.\cite{1}. Equation (3) has two contributions. The first one accounts for cooling due to endothermic dissociation and heating due to exothermic recombination reactions. The second contribution corresponds to background heating of the gas caused, e.g., by off-resonant scattering of the dipole-trap light. Equations (1) and (2) are coupled via the cloud sizes $\sigma_{r(ax)} = \sqrt{k_B T / m_M \omega_{r(ax)}^2}$ to the temperature equation (3).

The results of a corresponding calculation at 709G are shown in fig. S1 and are in very good agreement with the experimental data. The values of the parameters $C_2$ and $R_2$ are the same as in the main text. $C_H = (3.0 \pm 1.0) \times 10^{-7}$ s$^{-1}$ is mainly determined by the long-time evolution of the cloud size (see fig. S1d,e).

The total particle number in fig. S1c) exhibits the losses caused by the inelastic dimer-dimer collisions and agrees well with the experimental measurements. The temperature in fig. S1d) first decreases slightly due to endothermic dissociation after the heat pulse and then increases again due to the dipole-laser induced photodissociation. Figure S1e) shows the calculated cloud width $\sigma_{ax}$ as determined by the temperature $T$. It agrees well with the measurements (green circles) if
we average over the small-amplitude collective oscillations which have been excited by the initial heat pulse.

**Thermometry**

Within the parameter range of our experiments the molecular and atomic density distributions are each well described by that of a non-interacting thermal gas located in a harmonic trap. The axial sizes of the molecular and atomic clouds are given by $\sigma_{ax} = \sqrt{\frac{k_B T}{m \omega_{ax}^2}}$ and $\sigma_{ax,A} = \sqrt{2}\sigma_{ax}$, respectively. Because the axial trapping frequency $\omega_{ax}$ is precisely known for our setup, we can determine the temperature $T$ by measuring the molecular or atomic cloud size. These cloud sizes are extracted from images of the mixed atom/ molecule clouds after careful analysis, for which we also determine the atom fraction $N_A/N_{tot}$ of the cloud. Figure S2 shows a calculated typical example for the 1D density distributions (where the transverse directions have been integrated out) for atoms $n_A$, molecules $n_M$ and both $n_{tot} = 2n_M + n_A$.

**Rescaling the measured $C_2$ to a constant temperature**

Table S1 is the list of temperatures at which the $C_2$ measurements in fig. S3 are taken. The statistical uncertainty of the temperatures is around $\Delta T = 0.08\,\mu\text{K}$. The temperatures increase with decreasing scattering length $a$. This temperature change is a result of the way we prepare the sample. In particular, the magnetic field ramp to the target field takes place within a $21\,\mu\text{K} \times k_B$ deep trap which prevents further evaporative cooling. With decreasing $a$, the binding energy of the dimers increases and therefore for a given temperature the equilibrium molecule fraction increases. The corresponding molecular association, however, heats the sample.
Figure S1. **Model calculation for the evolution of the atom/molecule system.** Results from the coupled differential equations (1-3) (continuous lines). Plot symbols show experimental data for 709G. For details see text.
Figure S2. **Calculated 1D density distribution for a thermal cloud of atoms and molecules.** In a harmonic potential non-interacting atoms and molecules exhibit a Gaussian density distributions \( n_A \) and \( n_M \), respectively, of which the widths differ by a factor of \( \sqrt{2} \). The total density distribution is the sum \( n_{\text{tot}} = 2n_M + n_A \). Here, the atom fraction \( N_A/N_{\text{tot}} \) is 0.6.
Bourdel, T. et al. Experimental Study of the BEC-BCS Crossover Region in Lithium 6. *Phys. Rev. Lett.* **93**, 050401 (2004).