Symmetry Breaking in Sticky Collisions between Ultracold Molecules

Marijn P. Man, Gerrit C. Groenenboom, and Tijs Karman*
Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, Netherlands

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Ultracold molecules undergo "sticky collisions" that result in loss even for chemically nonreactive molecules. Sticking times can be enhanced by orders of magnitude by interactions that lead to nonconservation of nuclear spin or total angular momentum. We present a quantitative theory of the required strength of such symmetry-breaking interactions based on classical simulation of collision complexes. We find static electric fields as small as 10 V/cm can lead to nonconservation of angular momentum, while we find nuclear spin is conserved during collisions. We also compute loss of collision complexes due to spontaneous emission and absorption of black-body radiation, which are found to be slow.

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Ultracold molecules are promising for the realization of quantum simulation with tunable anisotropic long-range interactions [1–4], quantum computation [5–8], precision measurement [9,10], and the exploration of chemistry in a coherent quantum mechanical regime [11–15]. Unfortunately, the realization of these prospects has been hampered by universal collisional losses that occur in short-range encounters between molecules. These collisional losses limit the lifetime of ultracold molecular gases [12,16–19], limit our ability to collisionally cool molecules to high phase-space densities [20–24], and spoil Feshbach resonances that could otherwise form a control knob to tune interactions [25–28]. Initially, collisional losses were attributed to chemical reactions [12,29], but similar loss has been observed for nonreactive species [16–19], and therefore it is not fully understood what causes or how one might eliminate collisional loss.

Pioneering work by Mayle *et al.* [30,31] has proposed that collisions between ultracold molecules might be "sticky." Collision complexes have a high density of states, yet at ultracold temperatures can only dissociate in a single scattering channel. The idea put forward is that the collision complexes will chaotically explore available phase space, leading to excessively long sticking times determined by the density of states through Rice-Ramsperger-Kassel-Marcus (RRKM) theory. During these sticky collisions the molecules are vulnerable to collisions with a third body [30–32] or photoexcitation by the trapping laser [33]. This Letter has shaped the way the field thinks about collisional loss [34–37], although the debate is not settled on even the order of magnitudes of sticking times [38], nor on what physical loss processes might occur during that time.

Some of the present authors have proposed a theoretical framework to compute the density of states of ultracold collision complexes [32], and the rate of loss by photoexcitation of these complexes by the trapping laser [33]. These predictions were later confirmed quantitatively by two independent experiments using reactive KRb molecules [39] and nonreactive RbCs [40]. These experiments used modulated optical dipole traps, which maintain a time-averaged trapping potential while the dark time, during which the modulated trap is off, can exceed the collision complex's sticking time. This reduced photoexcitation loss even though the loss rate is saturated with light intensity when the trap light is on. Subsequent experiments on NaK and NaRb molecules, however, could not observe such suppression of collisional loss in a modulated trap [41], nor could collisional loss be eliminated by trapping the molecules in a repulsive box potential [42]. These observations remain unexplained, and form the main motivation for the present study.

It has been speculated that the sticking time could be enhanced by orders of magnitude by symmetry breaking that leads to the nonconservation of otherwise conserved quantum numbers, as this would drastically increase the effective phase-space volume that collision complexes explore ergodically. In particular, total angular momentum is strictly conserved *only* in the absence of external fields. Using the methods of Ref. [32] one can compute sticking times in the two limiting cases that total angular momentum is either strictly conserved or completely scrambled, but it is unclear at what external field strengths the transition between these limits occurs. Similarly, there are hints that nuclear spin degrees of freedom do not participate in the collision dynamics [14], but it is unclear for which molecules and under which conditions this is the case. Another possible explanation is that there exist additional loss mechanisms that limit the lifetime of collision complexes in the dark. It is, however, difficult to conclusively rule out *all possible* loss mechanisms.

In this Letter, we develop classical simulations of ultracold collision complexes. First, we show the simulated dynamics is consistent with chaotic dynamics and RRKM

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theory. Next, we study the effect of a finite electric field. Because of the dynamics of a collision complex, its dipole moment fluctuates rapidly. The autocorrelation function of these fluctuations determines the coupling between different total-angular-momentum states. We find static electric fields as small as 10 V/cm can lead to nonconservation of angular momentum. We also apply the formalism to nuclear spin couplings, and find nuclear spin states are conserved during the sticking time in NaK + NaK and RbCs + RbCs collisions. Finally, we apply the dipole autocorrelation function to compute loss of collision complexes by spontaneous emission and absorption of blackbody radiation. Both processes result in slow loss.

We perform classical simulations of the sticky ultracold collision complexes NaK + K, NaK + NaK, and RbCs + RbCs, as illustrated in Fig. 1(a) and explained in detail in Supplemental Material [43]. In short, we model the interactions using diatomics-in-molecules [43,79], which describes spin-dependent pairwise interactions between all atoms. The trajectories were initialized with molecules at their equilibrium bond length, for random orientations, and without vibrational or rotational kinetic energy, ensuring zero total angular momentum. The radial kinetic energy was chosen such that the total energy equaled the lowest dissociation limit. After a short thermalization time, we then simulated classical trajectories using a fourth-order symplectic propagator, which ensures conservation of phase-space volume and long-term numerical stability.

First, we investigate whether the simulated dynamics of the collision complexes is consistent with RRKM theory, as has been proposed by Mayle *et al.* [30,31]. The central result in RRKM theory is that the time spent in a phase-space region is given by

$$\tau_S^{\mathrm{RRKM}} = \frac{2\pi\hbar\rho_S}{N_S}, \tag{1}$$

where ρ_S is the density of states in that region, and N_S is the number of states at the boundary, which is known as the dividing surface. Applied to ultracold collisions where at dissociation there is only a single open channel $N_S = 1$, this yields the sticking time $\tau_{\mathrm{stick}}^{\mathrm{RRKM}} = 2\pi\hbar\rho_S$. Furthermore, there exists a clear separation of length scales of the complex, where the density of states ρ_S is supported by intermolecular separations R shorter than tens of Bohr radii [43], and the length scale of long-range interactions of hundreds of Bohr radii. Hence, one can unambiguously define a suitable dividing surface at intermediate R.

When simulating the dynamics classically, however, at zero collision energy $N_S \to 0$, not $N_S \to 1$, as the dividing surface is moved outward. Hence, one cannot converge the calculation by moving the dividing surface outward. Instead, we pick a dividing surface at a convenient distance $R_S \simeq 20\ a_0$. We then observe that the mean time elapsed

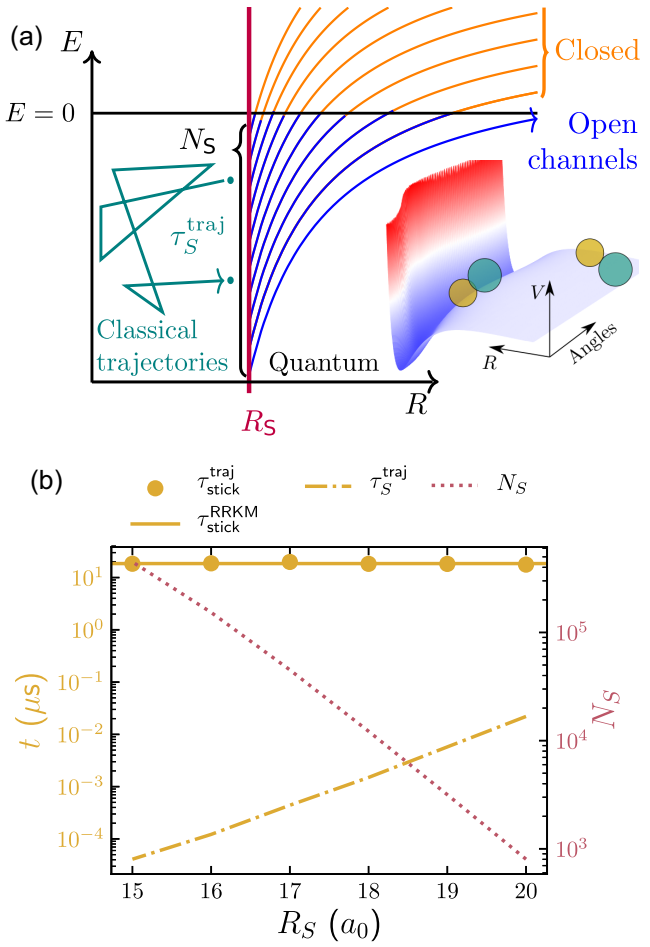

FIG. 1. Classical simulations of ultracold sticky collisions. Panel (a) shows schematically the classical simulations on a simple but realistic high-dimensional potential energy surface. After a typical time, τ_S^{traj}, the classical trajectory crosses the dividing surface $R = R_S$. At this surface, $N_S \gg 1$ collision channels are energetically accessible. We estimate the physical sticking time in ultracold collisions, where only a single collision channel is open, by correcting as $\tau_{\mathrm{stick}}^{\mathrm{traj}} = N_S\tau_S^{\mathrm{traj}}$. Panel (b) demonstrates quantitatively the steep dependence of τ_S^{traj} and N_S on the position of the dividing surface R_S and that the sticking time estimated from classical trajectories $\tau_{\mathrm{stick}}^{\mathrm{traj}}$ is independent of R_S and in quantitative agreement with sticking times obtained from phase-space integrals $\tau_{\mathrm{stick}}^{\mathrm{RRKM}}$.

before the trajectory crosses the dividing surface τ_S^{traj} becomes consistent with Eq. (1) if we account for the larger number of states N_S at the dividing surface, which is computed independently as a phase space integral. By extrapolating to the physical case where $N = 1$, we recover sticking times $\tau_{\mathrm{stick}}^{\mathrm{traj}} = N_S\tau_S^{\mathrm{traj}}$, in agreement with RRKM predictions based on density of states computed independently using phase-space integrals, see Fig. 1(b). This analysis provides support for the physical picture proposed by Mayle *et al.* [30,31] of classically chaotic dynamics, as subsequently assumed in further work [34–37].

Our approach has the remarkable advantage that we can study sticking times that are orders of magnitude larger than the time simulated.

Based on the above analysis, we caution sticking times cannot be extracted directly from classical simulations of sticking dynamics without accounting for the effective number of states at the dividing surface [80,81], which is furthermore impacted by inclusion of a finite collision energy, zero-point energy, or the numerically imperfect conservation of energy [43].

We now turn our attention to the nonconservation of quantum numbers by a symmetry-breaking perturbation. Following Feingold and Peres [82], transition moments of $\hat{A}$ between energy eigenstates in a classically chaotic system can be related to fluctuations of the classical observable $A(t)$ in a microcanonical ensemble. These fluctuations are quantified by the autocorrelation function (ACF) and the coupling between energy eigenstates is given by

$$|\langle i|\hat{A}|j\rangle|^2 = \frac{S_A(E,\omega_{ij})}{\hbar\rho}, \tag{2}$$

where

$$S_A(E,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle A(0)A(t')\rangle \exp(i\omega t')dt' \tag{3}$$

is the Fourier transform of the coupling's ACF that is computed classically, $\langle\cdots\rangle$ indicates a microcanonical ensemble average, and $\hbar\omega_{ij}$ is the energy difference between energy level i and j. We use the static limit $S_A(E,\omega) \approx S_A(E,0)$ because the typical transition frequency, in the order of $1/h\rho$, is much smaller than $1/\tau_{\mathrm{ACF}}$, where τ_{ACF} is a typical timescale for the decay of the ACF. The static limit $S_A(E,0)$ is simply the time integral of the ACF, and roughly in the order of $\langle A^2\rangle\tau_{\mathrm{ACF}}$. The mean magnitude of the coupling between energy eigenstates is then in the order of $A\sqrt{\tau_{\mathrm{ACF}}/\tau_{\mathrm{stick}}}$, which is hand-wavingly interpreted as the magnitude of the bare coupling A that is dynamically reduced if fluctuations of A are fast compared to the sticking time.

We specialize the discussion to coupling between J and $J' = J \pm 1$ states by the Stark interaction $\hat{A} = -\hat{\boldsymbol{d}}\cdot\boldsymbol{E}$ between the complex' dipole moment $\boldsymbol{d}$ and an external static electric field $\boldsymbol{E}$. We simulated dipole ACFs for NaK + K, NaK + NaK, and RbCs + RbCs collision complexes in zero field, see Supplemental Material for details [43]. The resulting ACFs are shown in Fig. 2.

Following Leitner *et al.* [83], we characterize the transition from J conservation to nonconservation using a dimensionless parameter,

$$\Omega = (\rho_0 + \rho_1)\langle \hat{H}^2_{0,1}\rangle^{1/2}, \tag{4}$$

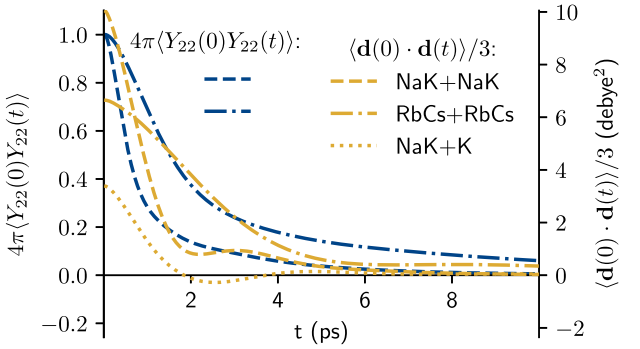

FIG. 2. Autocorrelation functions (ACFs). Dipole and spherical-harmonic ACFs for NaK + K, NaK + NaK, and RbCs + RbCs sticky collisions.

i.e., the root-mean-square coupling between $J = 0$ and 1 in units of the mean level spacing. At $\Omega \ll 1$ angular momentum is conserved and the sticking time is set by the $J = 0$ density of states, whereas at $\Omega \gg 1$ angular momentum is scrambled and the sticking time determined by the total density of states. At intermediate Ω, we calculate the distribution of time delays as described in detail in Supplemental Material [43]. This distribution is then fit with an effective density of states ρ_{eff} that is intermediate between these two extremes. As shown in Fig. 3, we find the effective density of states increases from $\rho_{J=0}$ at low fields, and approaches the total density of states at high field, as expected. The transition occurs around $\Omega = 1$, where the Stark coupling is comparable to the level spacing. The electric field at which this occurs in different systems depends strongly on the sticking time, which scales

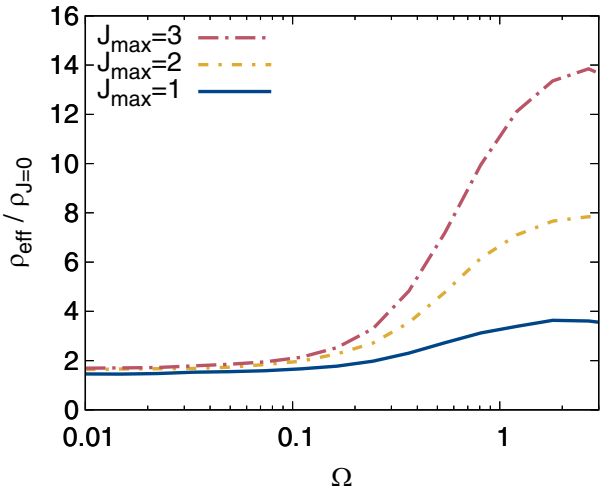

FIG. 3. Effective density of states as determined by fitting the distribution of sticking times, see Supplemental Material [43]. The dimensionless parameter Ω represents the Stark interaction in units of the level spacing, and hence effectively represents the electric field. The total density of states increases as $(1 + J_{\mathrm{max}})^2$ for large Ω, but the transition to J conservation consistently occurs around $\Omega = 1$ irrespective of the value of J_{max}.

TABLE I. Summary of numerical results. The static limits of the Fourier transform of the dipole and spherical harmonic ACFs, $S_d(0,0)$ and $S_{Y_2}(0,0)$, are listed. From this we determine the electric field around which the transition to nonconservation of total angular momentum occurs, $E_{\Omega=1}$, and find $\Omega_{\text{nucl.spin}} \ll 1$ indicating nuclear spin is conserved in sticky collisions. We also list the rates of spontaneous emission and absorption of black-body radiation. These results are subject to the ambiguity in the precise position of the transition as well as the uncertainty in the available interaction potentials, see Supplemental Material [43].

System	$S_d(0,0)$ (Debye^2 ps)	$E_{\Omega=1}$	$S_{Y_2}(0,0)$ (fs)	$\Omega_{\text{nucl.spin}}$	Γ_{spont} (s^{-1})	$\Gamma_{\text{black body}}$ (s^{-1})
NaK + K	1.2	14.8 kV/cm			0.015	0.082
NaK + NaK	3.7	48 V/cm	28	0.003	0.049	0.26
RbCs + RbCs	6.1	3.7 V/cm	71	0.06	0.0023	0.030

steeply with the masses and the number of degrees of freedom. For NaK + K this amounts to an electric field of ~10 kV/cm, whereas for sticky collisions between typical diatomic polar molecules electric fields in the order of ~10 V/cm break total angular momentum conservation, as summarized in Table I.

In Supplemental Material [43] we consider three alternative approaches to determine the transition to J nonconservation. First, we use a random matrix theory description of the short-range Hamiltonian, where we observe the level-spacing statistics as a function of the electric field. With increasing field strength, we observe a transition from Poisson to Wigner-Dyson statistics roughly around $\Omega = 1$, consistent with the above analysis. Second, we employ the framework of Ref. [37] to use this random matrix theory description to compute a collisional loss rate. We set the short-range loss Γ such that $\Gamma\rho_{J=0} \ll 1$, which results in a small collisional loss rate. As we apply an external electric field, the *effective* density of states increases and a transition can be observed in the collisional loss rate as $\Gamma\rho_{\text{eff}} \approx 1$. Also this transition occurs roughly around $\Omega = 1$. Finally, we directly simulated the classical dynamics in an external field. While J may no longer be conserved during the complex' sticking time, it may be conserved during the short durations we can actually simulate. Hence, our approach is to record the classical total angular momentum $J(t)$ during the simulation, and fit to $J \propto \sqrt{t}$, consistent with diffusion in total angular momentum. We then solve for the electric field strength at which $J(t)$ diffuses by one quantum during the sticking time, which is once again roughly consistent with $\Omega = 1$ seen in the other approaches.

The predicted electric field strengths can be tested in experiments, and are consistent with observations so far. In the RbCs experiment of Ref. [40], which yielded sticking times consistent with angular momentum conservation, an upper limit to the electric field is 7 V/cm [84]. Similarly, in the KRb experiment of Ref. [39], a static field of 17 V/cm was present, which should not break angular momentum conservation given the sticking time is shortened by 3 orders of magnitude due to chemical reactions.

We emphasize that we have here described the effect of a static electric field on the short-range physics. This is complimentary to a recent study of the effect of external fields on the long-range physics [36]. The effects on both the long-range and short-range physics can be described in a unified manner [34,37].

Having calculated the dipole autocorrelation function we are also in a position to discuss absorption or emission of far IR radiation by collision complexes. Figure 4 shows the absorption spectrum of black-body radiation at 293 K, and the spectrum of spontaneous emission. The rates of both processes are on the order of 0.1 s^{-1}, see Table I, and can be ruled out on the timescale of sticky collisions.

Finally, we apply the formalism developed here to the conservation of the nuclear spin state during a collision. For simplicity, we limit the discussion to the strongest hyperfine interaction. For RbCs this is the quadrupole coupling of the Rb nuclear spin $i = 3/2$ to the electric field gradient. Apart from constants, this takes the form $[[\hat{i} \otimes \hat{i}]^{(2)} \otimes Y^{(2)}(\hat{r})]^{(0)}$, where $\hat{i}$ is a nuclear spin operator, $[\hat{A} \otimes \hat{B}]^{(k)}$ is a rank-k tensor product, and $Y^{(2)}(\hat{r})$ is a tensor of spherical harmonics depending on the polar angles of the

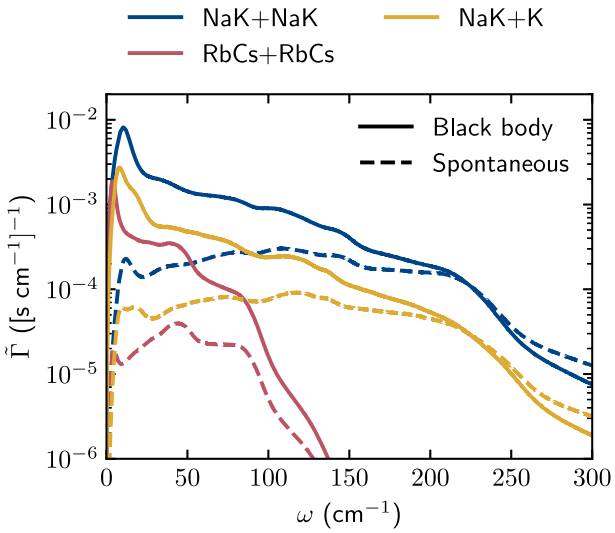

FIG. 4. Spectrum of spontaneous emission and absorption of black-body radiation at 293 K. The integrated intensity yields the loss rate, which is in the order of 0.1 s^{-1} and can essentially be excluded during sticky collisions, see Table I.

molecular axis $\hat{r}$. As with the dipole moment before, the dynamics of the collision complex rapidly reorients the molecular axis, resulting in a fluctuating coupling for the nuclear spin. The fluctuations are characterized by the ACF of the spherical harmonics, which determines the coupling from an initial spin state, say $m_i = 3/2$, to $m_i' = 1/2$ and $-1/2$. The $|\Delta m_i| \leq 2$ selection rule results from the second-rank coupling, which also changes the mechanical angular momentum from $J = 0$ to $J' = 2$. Numerical results for the relevant ACFs are shown in Fig. 2. From our simulations shown in Fig. 3 we can then immediately conclude nuclear spin is conserved for $\Omega \ll 1$. For RbCs, using hyperfine coupling constants form the literature and the simulated autocorrelation function of the spherical harmonics, we find $\Omega \approx 0.06$ such that nuclear spin remains conserved. A similar analysis accounting for the K nuclear quadrupole coupling in NaK + NaK complexes yields $\Omega = 0.003$, see Table I. This is in qualitative agreement with experimental sticking times that match theory assuming spin conservation [39,40], and consistent with spin-conservation in KRb + KRb collisions [14], although recent results in RbCs collisions suggest the sticking time might be hyperfine state dependent [85]. The approach developed here opens the door to subsequent studies accounting for all hyperfine couplings, their interaction-induced variations [86], and to explore the case of nonzero electronic spin where the fine-structure couplings may be orders of magnitude larger.

In conclusion, we have developed classical simulations of sticky collisions between ultracold molecules. The dynamics is consistent with RRKM theory and the sticking times predicted previously. We show how the nonconservation of nearly good quantum numbers (such as total angular momentum) can be calculated using the autocorrelation function of a perturbation (such as coupling to an E field). Static electric fields as small as 10 V/cm are found to lead to nonconservation of total angular momentum. The same dipole ACF can be used to study loss of collision complexes by spontaneous emission or absorption of blackbody radiation, which we conclude is slow. In addition, we show how the same method may be applied to the nonconservation of nuclear spin, suggesting the nuclear spin is conserved in sticky collisions, tentatively in agreement with observations. The framework presented here creates new possibilities to quantitatively study loss processes in ultracold collision complexes. By understanding the sticking times and loss processes quantitatively, we can hope to eliminate collisional loss of ultracold molecules which will aid the creation of long-lived molecular quantum gases, collisional cooling, and support Feshbach resonances that enable control of short-range interactions. The method employed here is quite general may also be used to efficiently simulate rare events in other areas of physics.

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*tkarman@science.ru.nl

[1] A. Micheli, G. K. Brennen, and P. Zoller, Nat. Phys. **2**, 341 (2006).
[2] H. P. Büchler, E. Demler, M. Lukin, A. Micheli, N. Prokof'Ev, G. Pupillo, and P. Zoller, Phys. Rev. Lett. **98**, 060404 (2007).
[3] N. R. Cooper and G. V. Shlyapnikov, Phys. Rev. Lett. **103**, 155302 (2009).
[4] L. D. Carr, D. DeMille, R. V. Krems, and J. Ye, New J. Phys. **11**, 055049 (2009).
[5] D. DeMille, Phys. Rev. Lett. **88**, 067901 (2002).
[6] S. F. Yelin, K. Kirby, and R. Côté, Phys. Rev. A **74**, 050301 (R) (2006).
[7] K.-K. Ni, T. Rosenband, and D. D. Grimes, Chem. Sci. **9**, 6830 (2018).
[8] A. M. Kaufman and K.-K. Ni, Nat. Phys. **17**, 1324 (2021).
[9] V. Andreev *et al.* (ACME Collaboration), Nature (London) **562**, 355 (2018).
[10] C. Ho, J. Devlin, I. Rabey, P. Yzombard, J. Lim, S. Wright, N. Fitch, E. Hinds, M. Tarbutt, and B. Sauer, New J. Phys. **22**, 053031 (2020).
[11] R. V. Krems, Phys. Chem. Chem. Phys. **10**, 4079 (2008).
[12] S. Ospelkaus, K. K. Ni, D. Wang, M. H. G. de Miranda, B. Neyenhuis, G. Quéméner, P. S. Julienne, J. L. Bohn, D. S. Jin, and J. Ye, Science **327**, 853 (2010).
[13] Y. Liu, M.-G. Hu, M. A. Nichols, D. Yang, D. Xie, H. Guo, and K.-K. Ni, Nature (London) **593**, 379 (2021).
[14] M.-G. Hu, Y. Liu, M. A. Nichols, L. Zhu, G. Quéméner, O. Dulieu, and K.-K. Ni, Nat. Chem. **13**, 435 (2021).
[15] Y. Liu and K.-K. Ni, Annu. Rev. Phys. Chem. **73**, 73 (2022).
[16] T. Takekoshi, L. Reichsöllner, A. Schindewolf, J. M. Hutson, C. R. Le Sueur, O. Dulieu, F. Ferlaino, R. Grimm, and H. C. Nägerl, Phys. Rev. Lett. **113**, 205301 (2014).
[17] P. K. Molony, P. D. Gregory, Z. Ji, B. Lu, M. P. Köppinger, C. R. Le Sueur, C. L. Blackley, J. M. Hutson, and S. L. Cornish, Phys. Rev. Lett. **113**, 255301 (2014).
[18] M. Guo, B. Zhu, B. Lu, X. Ye, F. Wang, R. Vexiau, N. Bouloufa-Maafa, G. Quéméner, O. Dulieu, and D. Wang, Phys. Rev. Lett. **116**, 205303 (2016).
[19] J. W. Park, S. A. Will, and M. W. Zwierlein, Phys. Rev. Lett. **114**, 205302 (2015).
[20] H. Son, J. J. Park, W. Ketterle, and A. O. Jamison, Nature (London) **580**, 197 (2020).
[21] G. Valtolina, K. Matsuda, W. G. Tobias, J.-R. Li, L. De Marco, and J. Ye, Nature (London) **588**, 239 (2020).
[22] K. Matsuda, L. De Marco, J.-R. Li, W. G. Tobias, G. Valtolina, G. Quéméner, and J. Ye, Science **370**, 1324 (2020).
[23] J.-R. Li, W. G. Tobias, K. Matsuda, C. Miller, G. Valtolina, L. De Marco, R. R. Wang, L. Lassablière, G. Quéméner, J. L. Bohn *et al.*, Nat. Phys. **17**, 1144 (2021).
[24] A. Schindewolf, R. Bause, X.-Y. Chen, M. Duda, T. Karman, I. Bloch, and X.-Y. Luo, Nature (London) **607**, 677 (2022).
[25] H. Yang, D.-C. Zhang, L. Liu, Y.-X. Liu, J. Nan, B. Zhao, and J.-W. Pan, Science **363**, 261 (2019).
[26] H. Yang, X.-Y. Wang, Z. Su, J. Cao, D.-C. Zhang, J. Rui, B. Zhao, C.-L. Bai, and J.-W. Pan, Nature (London) **602**, 229 (2022).

[27] H. Son, J. J. Park, Y.-K. Lu, A. O. Jamison, T. Karman, and W. Ketterle, Science **375**, 1006 (2022).
[28] Z. Su, H. Yang, J. Cao, X.-Y. Wang, J. Rui, B. Zhao, and J.-W. Pan, Phys. Rev. Lett. **129**, 033401 (2022).
[29] Z. Idziaszek and P. S. Julienne, Phys. Rev. Lett. **104**, 113202 (2010).
[30] M. Mayle, B. P. Ruzic, and J. L. Bohn, Phys. Rev. A **85**, 062712 (2012).
[31] M. Mayle, G. Quéméner, B. P. Ruzic, and J. L. Bohn, Phys. Rev. A **87**, 012709 (2013).
[32] A. Christianen, T. Karman, and G. C. Groenenboom, Phys. Rev. A **100**, 032708 (2019).
[33] A. Christianen, M. W. Zwierlein, G. C. Groenenboom, and T. Karman, Phys. Rev. Lett. **123**, 123402 (2019).
[34] J. F. E. Croft, J. L. Bohn, and G. Quéméner, Phys. Rev. A **102**, 033306 (2020).
[35] J. F. E. Croft, J. L. Bohn, and G. Quéméner, arXiv: 2111.09956.
[36] G. Quéméner, J. F. Croft, and J. L. Bohn, Phys. Rev. A **105**, 013310 (2022).
[37] A. Christianen, G. C. Groenenboom, and T. Karman, Phys. Rev. A **104**, 043327 (2021).
[38] M. A. Nichols, Y.-X. Liu, L. Zhu, M.-G. Hu, Y. Liu, and K.-K. Ni, Phys. Rev. X **12**, 011049 (2022).
[39] Y. Liu, M.-G. Hu, M. A. Nichols, D. D. Grimes, T. Karman, H. Guo, and K.-K. Ni, Nat. Phys. **16**, 1132 (2020).
[40] P. D. Gregory, J. A. Blackmore, S. L. Bromley, and S. L. Cornish, Phys. Rev. Lett. **124**, 163402 (2020).
[41] P. Gersema, K. K. Voges, M. Meyer zum Alten Borgloh, L. Koch, T. Hartmann, A. Zenesini, S. Ospelkaus, J. Lin, J. He, and D. Wang, Phys. Rev. Lett. **127**, 163401 (2021).
[42] R. Bause, A. Schindewolf, R. Tao, M. Duda, X.-Y. Chen, G. Quéméner, T. Karman, A. Christianen, I. Bloch, and X.-Y. Luo, Phys. Rev. Res. **3**, 033013 (2021).
[43] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.129.243401 for a detailed description of the calculations, which includes Refs. [44–78].
[44] O. K. Rice and H. C. Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927).
[45] L. S. Kassel, J. Phys. Chem. **32**, 225 (1928).
[46] H. Eyring, J. Chem. Phys. **3**, 107 (1935).
[47] R. A. Marcus, J. Chem. Phys. **20**, 359 (1952).
[48] W. H. Miller, Acc. Chem. Res. **26**, 174 (1993).
[49] B. Gao, Phys. Rev. A **58**, 1728 (1998).
[50] I. Omelyan, I. Mryglod, and R. Folk, Comput. Phys. Commun. **146**, 188 (2002).
[51] A. Gerdes, M. Hobein, H. Knöckel, and E. Tiemann, Eur. Phys. J. D **49**, 67 (2008).
[52] A. Pashov, P. Popov, H. Knöckel, and E. Tiemann, Eur. Phys. J. D **46**, 241 (2008).
[53] S. Knoop, T. Schuster, R. Scelle, A. Trautmann, J. Appmeier, M. K. Oberthaler, E. Tiesinga, and E. Tiemann, Phys. Rev. A **83**, 042704 (2011).
[54] L. Li, S. F. Rice, and R. W. Field, J. Chem. Phys. **82**, 1178 (1985).
[55] O. Docenko, M. Tamanis, R. Ferber, H. Knöckel, and E. Tiemann, Phys. Rev. A **83**, 052519 (2011).
[56] M. Krauss and W. J. Stevens, J. Chem. Phys. **93**, 4236 (1990).
[57] C. Amiot and O. Dulieu, J. Chem. Phys. **117**, 5155 (2002).
[58] F. Xie, V. B. Sovkov, A. M. Lyyra, D. Li, S. Ingram, J. Bai, V. S. Ivanov, S. Magnier, and L. Li, J. Chem. Phys. **130**, 051102 (2009).
[59] M. Tomza, W. Skomorowski, M. Musiał, R. González-Férez, C. P. Koch, and R. Moszynski, Mol. Phys. **111**, 1781 (2013).
[60] H. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Comput. Mol. Sci. **2**, 242 (2012).
[61] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, T. Leininger, R. Lindh, A. W. Lloyd, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, K. Peterson, R. Pitzer, P. Pulay, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone, and T. Thorsteinsson.
[62] P. Fuentealba, H. Preuss, H. Stoll, and L. Von Szentpály, Chem. Phys. Lett. **89**, 418 (1982).
[63] L. von Szentpály, P. Fuentealba, H. Preuss, and H. Stoll, Chem. Phys. Lett. **93**, 555 (1982).
[64] P. Fuentealba, H. Stoll, L. von Szentpály, P. Schwerdtfeger, and H. Preuss, J. Phys. B **16**, L323 (1983).
[65] A. Christianen, T. Karman, R. A. Vargas-Hernández, G. C. Groenenboom, and R. V. Krems, J. Chem. Phys. **150**, 064106 (2019).
[66] G. E. Mitchell, A. Richter, and H. A. Weidenmüller, Rev. Mod. Phys. **82**, 2845 (2010).
[67] F. T. Smith, Phys. Rev. **118**, 349 (1960).
[68] T. Prosen, Ann. Phys. (N.Y.) **235**, 115 (1994).
[69] M. Wilkinson, J. Phys. A **20**, 2415 (1987).
[70] S. Hortikar and M. Srednicki, Phys. Rev. E **57**, 7313 (1998).
[71] R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).
[72] R. Gordon, Adv. Magn. Reson. **3**, 1 (1968).
[73] T. Brody, Lettere al Nuovo Cimento **7**, 482 (1973).
[74] S. Y. Buhmann, M. R. Tarbutt, S. Scheel, and E. A. Hinds, Phys. Rev. A **78**, 052901 (2008).
[75] B. H. Bransden and J. C. J., *Physics of Atoms and Molecules*, 2nd ed. (Pearson Education Limited, 2003).
[76] W. Press, S. Teukolsky, W. Vetterling, and B. Flannery, *Numerical Recipes: The Art of Scientific Computing*, Third Edition in C++ (Cambridge University Press, Cambridge, England, 2007).
[77] F. Harris, Proc. IEEE **66**, 51 (1978).
[78] J. Aldegunde and J. M. Hutson, Phys. Rev. A **96**, 042506 (2017).
[79] F. O. Ellison, J. Am. Chem. Soc. **85**, 3540 (1963).
[80] J. F. E. Croft and J. L. Bohn, Phys. Rev. A **89**, 012714 (2014).
[81] J. Kłos, Q. Guan, H. Li, M. Li, E. Tiesinga, and S. Kotochigova, Sci. Rep. **11**, 1 (2021).
[82] M. Feingold and A. Peres, Phys. Rev. A **34**, 591 (1986).
[83] D. M. Leitner, H. Köppel, and L. S. Cederbaum, Phys. Rev. Lett. **73**, 2970 (1994).
[84] S. L. Cornish (private communication).
[85] P. D. Gregory, J. A. Blackmore, M. D. Frye, L. M. Fernley, S. L. Bromley, J. M. Hutson, and S. L. Cornish, New J. Phys. **23**, 125004 (2021).
[86] K. Jachymski, M. Gronowski, and M. Tomza, Phys. Rev. A **106**, L041301 (2022).