PHYSICAL REVIEW LETTERS

Experimental Investigation of Ultracold Atom-Molecule Collisions

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Ultracold collisions between Cs atoms and Cs_2 dimers in the electronic ground state are observed in an optically trapped gas of atoms and molecules. The Cs_2 molecules are formed in the triplet ground state by cw photoassociation through the outer well of the $0_g^-(P_{3/2})$ excited electronic state. Inelastic atom-molecule collisions converting internal excitation into kinetic energy lead to a loss of Cs_2 molecules from the dipole trap. Rate coefficients are determined for collisions involving Cs atoms in either the $F = 3$ or $F = 4$ hyperfine ground state, and Cs_2 molecules in either highly vibrationally excited states ($v' = 32$–47) or in low vibrational states ($v' = 4$–6) of the $a\,^3\Sigma_u^+$ triplet ground state. The rate coefficients $\beta \sim 10^{-10}$ cm^3/s are found to be largely independent of the vibrational and rotational excitation indicating unitary limited cross sections.

At very low temperatures the elastic and inelastic scattering of particles is governed by quantum mechanical effects such as resonances or tunneling through barriers, since the de Broglie wavelength becomes comparable to the range of the interparticle interactions. With the advent of laser cooling techniques, ultracold atom-atom collisions have been studied intensively both experimentally and theoretically. Their understanding and control has been decisive for the rapid development of the field of quantum gases [1]. As a prominent example, the competition between elastic and inelastic collisions of trapped atoms determines the success of evaporative cooling for achieving atomic Bose-Einstein condensation [2]. Recently, the focus has been moving from pure atomic to ultracold atom-molecule and molecule-molecule collisions, which are highly relevant for the formation and stability of molecular Bose-Einstein condensates [3,4]. The investigation of atom-molecule scattering at very low temperatures forms the basis of the emerging field ultracold chemistry [5].

Theoretical studies show that ultracold atom-molecule collisions do not "freeze out" at low temperatures, as classical Langevin capture theory predicts, but feature instead significant rate coefficients at ultralow temperatures where only a few partial waves contribute [6–10]. The energy dependence of cross sections at low temperatures is predicted to be in good agreement with the Wigner threshold law [8–10]. Until now these calculations have been based on single potential energy surfaces. However, coupling of several low-lying potentials through conical intersections can lead to additional features in the rate coefficients through shape and Feshbach resonances [11]. Since the collision energy is much smaller than the energy spacing between internal states in the colliding atoms and molecules, the only inelastic processes to occur are collisional deexcitation and, for nonidentical atoms, reactive scattering followed by chemical rearrangement. At room temperature, the energy transfer from molecular vibration to translation and rotation is suppressed when the vibra-

tional level spacings are large compared to the translational temperature; i.e., the probability for deexcitation per collision is much smaller than unity [12,13]. In contrast, below 10^{-3} K Refs. [8–10] show that the inelastic rate coefficient for lithium, sodium, and potassium atom-diatom collisions is higher than the elastic rate coefficient and does not depend on temperature, again in agreement with the Wigner threshold law. In Refs. [6,7] the inelastic collision rate coefficient for $He-H_2$ and $H-H_2$ collisions is found to strongly increase with the vibrational quantum number. On the other hand, Stwalley [14] has recently argued that molecules in the highest vibrational levels near the dissociation threshold should feature very small inelastic collision rates. In addition to vibrational excitation, rotational quantum states may influence the rate of inelastic collisions, e.g., due to quasiresonant exchange of rotational and vibrational energy [15]. Clearly, experimental investigations are needed to reveal the collisional behavior of molecules at ultralow temperatures and to test quantum scattering calculations in the interesting transition region from the Wigner threshold regime to the Langevin regime.

Few experimental studies on ultracold atom-molecule collisions have been carried out so far. The possibilities are being limited by the difficulty in producing and trapping ultracold molecules simultaneously with cold atoms at sufficiently high densities. Successful storage of ultracold molecules has first been shown in an optical dipole trap [16] and recently in magnetic traps [17]. Cold collisions at a temperature of $T \sim 0.5$ K have been studied between He buffer gas-cooled CaF and He [18]. For ultracold Na_2 molecules formed through a Feshbach resonance, collision rate coefficients were determined for both atom-molecule and molecule-molecule collisions [19]. Similarly ultracold molecule-molecule collisions were observed for Cs_2 and a strong loss rate due to Feshbach-like resonances was observed [20]. These two experiments at ultralow temperatures probe molecules in the last bound vibrational level.

Here we present an experimental study of ultracold atom-molecule collisions involving molecules in deeply bound vibrational states. Cs ground state atoms and photo-associated Cs_2 molecules are stored together in an optical dipole trap. Rate coefficients are determined for exoergic atom-molecule collisions, observed through molecule loss, with Cs_2 in high-lying vibrational levels ($v' = 32$–47, bound by 1–24 cm^{-1}) and in low-lying levels ($v' = 4$–6, bound by 175–195 cm^{-1}) in the $a^3\Sigma^+$ triplet ground state [21,22]. We find for molecules in high-lying and low-lying states equally large rate coefficients, larger than the s-wave scattering limit. The inelastic rate coefficients for different Cs_2 rotational states coincide, which indicates that vibrational deexcitation dominates over rotational deexcitation in the collision. A significant increase in the deexcitation rate is found for collisions with Cs atoms in the $F = 4$ hyperfine level of the $^2S_{1/2}$ ground state as compared to $Cs(F = 3)$.

The measurements proceed as follows. An optical dipole trap, formed by the focus of a 120 W CO_2 laser (Synrad Evolution 100, waist ~ 90 μm) is loaded with $Cs(F = 3)$ atoms from a magneto-optical trap (MOT). We transfer $N_{at} \sim 2 \times 10^5$ Cs atoms into the dipole trap with a shot-to-shot variation of less than 5% at a typical mean density of $n_{at} = 10^{11}$ cm^{-3} and temperature $T = 60 \pm 20$ μK. The atom density is determined and the temperature estimated from a measurement of the $F = 4$ atom loss due to hyperfine-changing collisions [23] and atom-background gas collisions. The atoms are then optically pumped to $F = 4$ and about 5% of the atoms are transformed into molecules by photoassociation [24] with a cw Ti:sapphire laser (Coherent MBR110) applied with intensity ~ 600 W/cm^2. After 100 ms of photoassociation an equilibrium between formation and collision-induced loss has been reached, resulting in ~ 5000 molecules in the trap. Their temperature is estimated to be approximately equal to the atom temperature, i.e., 60 μK, and the mean density $n_{mol} \sim 3 \times 10^9$ cm^{-3}. Subsequently, the remaining atoms can be either optically pumped to the $F = 3$ hyperfine state ($>99\%$ efficiency with negligible atom loss), be pushed out of the trap with a resonant laser beam ($>99\%$ efficiency), or be left in the $F = 4$ state. By measuring the number of trapped molecules N_{mol} as a function of storage time τ we deduce the inelastic collision rate coefficient. Each measurement of $N_{mol}(\tau)$ is an average over typically 48 cycles. $N_{mol}(\tau = 0)$ is determined before and after each measurement to correct for drifts in the experiment, mainly small frequency drifts of the photoassocation laser. The error bars of the detected molecule number combine the corresponding statistical and correction uncertainties.

The molecules are detected via resonance-enhanced two-photon ionization using an unfocused pulsed dye laser beam (Radiant Dyes Narrowscan, ~ 10 mJ per pulse, wavelength 712.5 nm, and linewidth < 0.1 cm^{-1}). The Cs_2^+ ions are measured with a high resolution time-of-flight mass spectrometer [25]. The number of detected mole-

cules, calibrated from the signal of individual Cs_2^+ ions, is smaller than the number of trapped molecules due to the combined efficiencies of the ionization (10%) and detection (20%) [26]. This calibration does not influence the measured rate coefficients, which only depend on the relative intensity of the molecular signal. Ground state atoms can only be ionized by three-photon ionization. Therefore, the Cs^+ signal is suppressed as compared to the Cs_2^+ signal (see inset of Fig. 1).

The preparation of Cs_2 molecules in either high- or low-lying levels of the triplet ground state is performed by photoassociation through the $v = 6$ or $v = 79$ states, respectively, of the outer well of the $0_g^-\,(^2P_{3/2})$ potential [27]. The $v = 6$ state decays primarily to the states $v' = 32$–47, whereas for $v = 79$ mainly the low-lying states $v' = 4$–6 are populated [21,22]. In the $0_g^-(v = 6)$ state the rotational states are resolved and hence molecules can be formed in the $a^3\Sigma_u^+$ state in $(v', J' = 1)$ and $(v', J' = J, J \pm 1)$ when $J = 0$ and $J \neq 0$, respectively, ($|J - J'| = 0, 1$; $J = 0 \nrightarrow J' = 0$). In Fig. 1 we show examples of storage time measurements of $Cs_2(v' = 32$–$47)$ molecules with and without atoms in the trap. In the presence of atoms at a mean density of $9.1 \pm 0.4_{stat} \pm 2.4_{syst} \times 10^{10}$ cm^{-3} the molecule storage time is reduced by a factor of 7 as compared to the case without atoms, a clear indication of collision induced loss.

The collision induced molecule loss can be due to vibrational and rotational deexcitation of the molecules as well as a change of the molecular or atomic hyperfine ground state (for Cs in $F = 4$). In all cases the released energy largely exceeds the trap depth of ~ 2 mK for molecules and ~ 1 mK for atoms and hence both collision partners are lost from the trap with practically unity probability. Since the number of atoms N_{at} is much larger than N_{mol}, the evolution of N_{mol} can be described by a simple rate equation
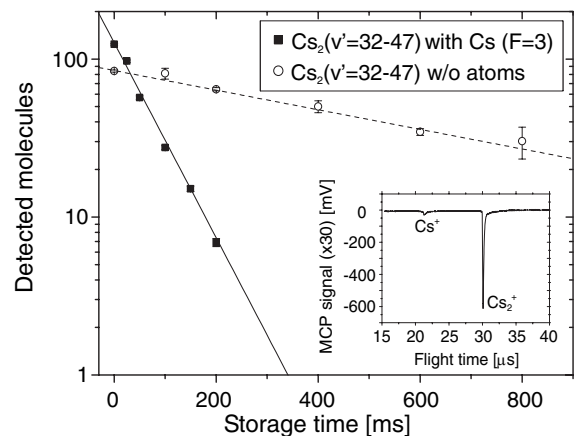

FIG. 1. Storage time measurement for $Cs_2(v' = 32$–$47)$ molecules with $Cs(F = 3)$ atoms in the dipole trap at a mean density of $n_{at} = 9.1 \pm 0.4_{stat} \pm 2.4_{syst} \times 10^{10}$ cm^{-3} (black filled squares) and with only molecules in the trap (circles). The lines represent fits to an exponential decay. Inset: Time-of-flight spectrum showing the Cs^+ and Cs_2^+ signals.

$$\dot{N}_{\mathrm{mol}} = -\left[\frac{8}{\sqrt{27}}\beta n_{\mathrm{at}}(t) + \Gamma_{\mathrm{mol}}\right]N_{\mathrm{mol}}, \qquad (1)$$

where β is the atom-molecule inelastic collision rate coefficient, Γ_{mol} is the loss rate due to molecule-background gas collisions and n_{at} is weakly time-dependent due to hyperfine-changing collisions [for $Cs(F = 4)$] and collisions of atoms with background gas. The factor of $8/\sqrt{27}$ accounts for the spatial averaging over atomic and molecular spatial distributions assuming equal atom and molecule temperature. This equation is strictly valid only for a single internal quantum state of the molecule, due to the general dependence of the rate coefficient on the quantum state. Therefore, we effectively obtain rate coefficients averaged over the populated quantum states. Molecule-molecule collisions are neglected in Eq. (1), because no significant molecule-molecule collision rate was observed when measuring the dependence of the molecular storage time on the initial number of molecules.

In the case of $F = 3$ atoms, n_{at} is constant since changes due to atom-background gas collisions (storage time ~ 5 s) can be neglected over the relevant molecule storage times. Thus, $N_{\mathrm{mol}}(t)$ is described by an exponential decay with loss rate $8\beta n_{\mathrm{at}}/\sqrt{27} + \Gamma_{\mathrm{mol}}$. In Fig. 2, this loss rate is shown for $Cs_2(v' = 32-47)$ as well as $Cs_2(v' = 4-6)$ at different $Cs(F = 3)$ atom densities. The density is varied by varying the MOT size before transfer into the dipole trap and the final detuning for cooling in optical molasses [24]. For $n_{\mathrm{at}} = 0$ all atoms are pushed out of the trap after photoassociation. The loss rate follows the expected linear dependence on atom density, thus confirming molecule loss due to atom-molecule collisions. From fitting a straight line the inelastic rate coefficients $\beta^{F=3}_{v'=32-47} = 0.96 \pm 0.02_{\mathrm{stat}} \pm 0.3_{\mathrm{syst}} \times 10^{-10}$ cm^3/s and $\beta^{F=3}_{v'=4-6} = 0.98 \pm 0.07_{\mathrm{stat}} \pm 0.3_{\mathrm{syst}} \times 10^{-10}$ cm^3/s are deduced (the systematic error is due to the uncertainty on n_{at} of which
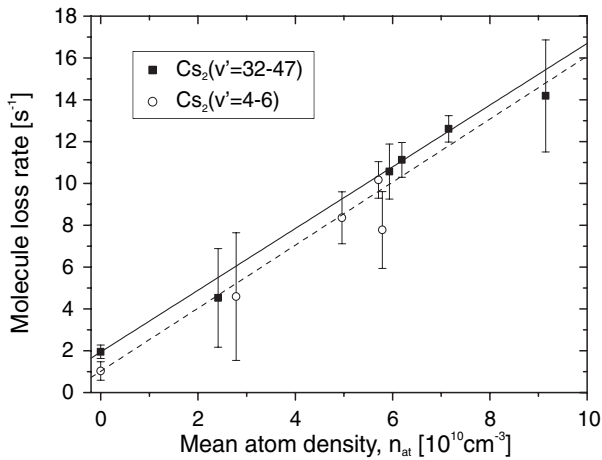

FIG. 2.   Molecule loss rate $8\beta n_{\mathrm{at}}/\sqrt{27} + \Gamma_{\mathrm{mol}}$ vs n_{at} for collisions between $Cs(F = 3)$ and $Cs_2(v' = 32-47)$ (solid squares) and $Cs_2(v' = 4-6)$ (circles). The straight lines represent fits discussed in the text (solid: $v' = 32-47$, dashed: $v' = 4-6$).

the ratio between collision rate coefficients is independent). Interestingly, these rate coefficients show no dependence on the Cs_2 vibrational level, even though they bridge many vibrational quantum numbers. This effect is further discussed below.

In order to investigate to what extent rotational deexcitation contributes to the molecule loss, we performed molecule storage time measurements for photoassociation via the rotational levels $0_g^-(v = 6, J = 0, 1, 2, 3, 4)$, thus populating different rotational levels $a^3\Sigma_u^+(v' = 32-47, J')$. If rotational deexcitation gave rise to a significant molecule loss we would expect a relatively low loss rate when $a^3\Sigma_u^+(v' = 32 - 47, J' = 0)$ is populated, i.e., for photoassociation to $J = 1$. However, we consistently find the rate coefficients for all rotational states J' to be equal within our experimental error. Thus, we conclude that the molecule loss is governed by vibrational deexcitation. Molecular hyperfine-changing collision rates are expected to be similar to atomic ones [23] and therefore about an order of magnitude smaller.

In contrast to the ultracold atom-molecule collisions, the collisions of the optically trapped molecules with the background gas at 300 K depend on the vibrational state, as seen in the loss rates $\Gamma_{\mathrm{mol}}(v' = 32-47) = 1.9(2)$ s^{-1} and $\Gamma_{\mathrm{mol}}(v' = 4-6) = 1.0(3)$ s^{-1} deduced from the fit. The faster loss for the higher vibrational levels may be attributed either to a larger geometric cross section for elastic collisions due to the larger average bond length or to the energetically open channel of collision induced dissociation (binding energy ~ 10 cm^{-1} for $v' = 32-47$ compared to ~ 185 cm^{-1} for $v' = 4-6$). In either case, this observation shows that the molecules are indeed selectively formed in either high-lying or low-lying vibrational states of the triplet ground state.

When molecules are stored with $Cs(F = 4)$ atoms, a time dependence of the atomic density has to be included due to hyperfine-changing atom-atom collisions [see Eq. (7) of Ref. [23]]. Solving Eq. (1) we find

$$N_{\mathrm{mol}}(t) = N_{\mathrm{mol}}(0)e^{-\Gamma_{\mathrm{mol}}t}[1 + 7Gn_{\mathrm{at}}(0)t/2]^{-16\beta/(7\sqrt{27}G)}, \qquad (2)$$

where $G = 1.1 \pm 0.3 \times 10^{-11}$ cm^3/s is the rate coefficient for hyperfine-changing collisions between $Cs(F = 4)$ atoms. Figure 3 shows a storage time measurement of $Cs_2(v' = 32-47)$ dimers together with a fit to Eq. (2). Several measurements at different atomic densities yield fitted rate coefficients independent of atom density as expected for atom-molecule collisions. Their average is $\beta^{F=4}_{v'=32-47} = 1.38 \pm 0.04_{\mathrm{stat}} \pm 0.4_{\mathrm{syst}} \times 10^{-10}$ cm^3/s. This rate coefficient is larger than $\beta^{F=3}_{v'=32-47}$, which can be attributed to the additional loss channel of hyperfine-changing collisions [23].

The measured rate coefficients are quite close to the ones predicted for Na-Na_2 and K-K_2 collisions [9,10] for low-lying vibrational levels in the respective $a^3\Sigma_u^+$ triplet ground states and comparable to the value found
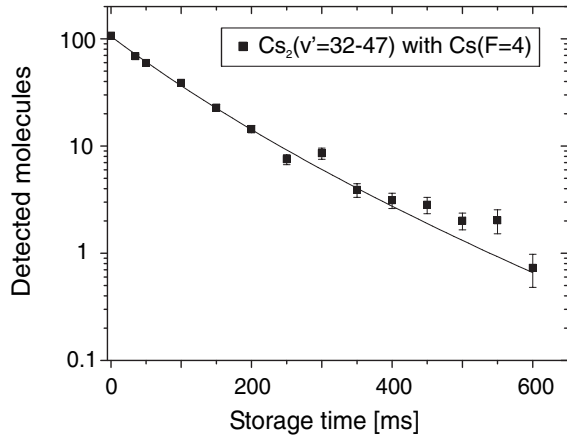
FIG. 3. Storage time measurement for $Cs_2(v' = 32\text{–}47)$ in collisions with $Cs(F = 4)$. Equation (2) is fitted to the data to obtain the inelastic rate coefficient.

in Ref. [19] for Na_2 formed via a Feshbach resonance. We do not, however, observe a strong increase of the inelastic rate coefficient with the vibrational quantum number, as predicted, e.g., for He-H_2 collisions [6]. It is illustrative to compare the measured inelastic rate coefficients to the inelastic s-wave collision limit, $\langle \sigma^{(0)} v \rangle \sim \sqrt{2\pi\hbar^4/(\mu^3 k_B T)}$, where $\sigma^{(0)} = \pi/k^2$ is the s-wave limit of the scattering cross section, $\hbar k$ the relative particle momentum, v the relative particle velocity, μ the reduced mass, and $\langle \ldots \rangle$ indicates an average over a Boltzmann distribution. For collisions between Cs and Cs_2 at $T = 60\ \mu K$ we obtain $1.7 \times 10^{-11}\ cm^3/s$, 6 times less than the measured rate coefficients. Since the lth partial wave at most contributes $(2l + 1)\sigma^{(0)}$ to the total scattering cross section, it is clear that p-wave as well as d-wave collisions play a significant role in the collisions. This observation agrees with p-wave and d-wave barrier heights, estimated as in Ref. [8], of 16 and 83 μK, respectively.

In conclusion, we have presented a quantitative experimental study of ultracold atom-molecule collisions with molecules in states well below the dissociation limit. We have determined rate coefficients for inelastic collisions between molecules in various rovibrational states and $Cs(F = 3)$ atoms and in one case also $Cs(F = 4)$ atoms at temperatures around 60 μK. The inelastic collisions are found to be governed by vibrational deexcitation and show no dependence on the rotational quantum number. The rate coefficients are about 6 times larger than the s-wave scattering limit, showing that p-wave as well as d-wave collisions contribute. In an improved setup containing a crossed dipole trap providing higher atomic and thus molecular densities, it will be possible to also study molecule-molecule collisions at ultralow temperatures. Interesting future experiments will comprise collisions and ultracold exchange reactions with mixed alkali species in an optical trap [28] and with molecules in a single internal quantum state, particularly molecules in $v = 0$ of the singlet or triplet ground state, which should have significantly longer trapping times due to the lack of vibrationally inelastic collisions [29,30]. With the development of high-resolution state-selective detection techniques, studies on state-to-state molecular reaction dynamics and quantum chemistry at ultralow temperatures seem to be within reach.

Note added.—We recently became aware that similar work with comparable results has been carried out simultaneously in the group of P. Pillet at the Laboratoire Aimé Cotton in Orsay, France [31].

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