POLAR MOLECULES NEAR QUANTUM DEGENERACY[*]

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The advent of a quantum degenerate gas of ground-state polar molecules opens the door to a wide range of scientific explorations. Novel molecular interactions, quantum-controlled chemical reactions, exotic phase transitions and strongly correlated states of matter are among a few prominent examples to be studied. We discuss recent experimental progresses at JILA, including the production of a high-density gas of ultracold KRb polar molecules in their absolute rovibrational ground state, coherent manipulations of the nuclear spin degrees of freedom, observations of barrier-less chemical reactions with the associated rates controlled by pure long-range, quantum mechanical effects, and control of inelastic and elastic collision cross sections via the tuning of the molecular dipole moment.

1. Introduction

Atomic gases prepared at ultralow temperatures have enabled many important scientific applications. Specifically, the exquisite control of atomic motion and their quantum states has allowed precision measurement to test fundamental physical principles, establishment of infrastructure for quantum information science, modeling of condensed matter systems, and study of novel quantum phenomena. So what is new with an ultracold gas of polar molecules [1]? Obviously extending our control capabilities from atomic gases to more complex molecular gases represents a trend and also a triumph of modern atomic, molecular, and optical physics. The vastly more complex energy level structure of molecules gives rise to unique and important opportunities for precision measurement. Meanwhile, preparing a molecular gas in the quantum regime represents a fundamentally new paradigm for the study of molecular interactions and chemical reactions. Complex and yet fundamental chemical reactions can now be studied and controlled from the first principles of quantum mechanics. Furthermore, the presence of long-range and anisotropic interactions

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in a quantum gas of polar molecules brings fundamentally new abilities to the study of strongly correlated systems where novel quantum phase transitions and new states of matter can be explored. A unique set of new phenomenology is expected for a dipolar quantum gas [2] and exotic condensed matter systems can be modeled and simulated [3].

The importance of ultracold molecules was realized early on and many different approaches have been adopted to produce dense samples of ground state polar molecules. Included under the general category of direct cooling of molecules are buffer gas cooling [4], deceleration of a molecular beam via an electric [5], magnetic [6], or optical field [7], and kinematic cooling via collisions [8]. These diverse techniques working on a variety of polar molecules have so far produced cold samples with a phase space density below 10^{-12}, obviously far from quantum degeneracy. Laser cooling of molecules have been proposed [9], but has not been implemented due partly to the complex energy level structure and partly to the lack a sufficiently dense sample of molecules. Photoassociation of a pair of ultracold atoms into a molecule is categorized as an indirect cooling method. Production of ultracold ground-state polar molecules was achieved [10], but with a phase space density also below 10^{-12}. The observation of dipolar interactions in a molecular gas requires the dipolar interaction energy to be comparable to the kinetic energy. This requirement can be fulfilled only when the phase space density of a polar molecular gas reaches near unity, namely a polar molecular gas near quantum degeneracy.

We recently combined a dual-species quantum degenerate quantum gas and coherent state transfer to produce a near quantum-degenerate polar molecular gas in the absolute rovibrational ground state [11]. A heteronuclear quantum gas mixture of fermionic ^{40}K and bosonic ^{87}Rb is first efficiently converted into weakly bound Feshbach molecules in a single quantum state. In the second step, a pair of highly phase-coherent Raman laser fields precisely and efficiently transfers the population from the weakly bound Feshbach state to the zero-vibration and zero-rotation quantum level in the singlet electronic ground-state, resulting in a final molecular phase space density of 0.06.

We have further gained a fully coherent control of the last remaining degree of freedom, namely the nuclear spin states of the molecules. We have demonstrated the capability of preparing a rovibronic ground-state molecular quantum gas in a single hyperfine state and, in particular, in the absolute lowest energy quantum state [12]. This latest advance has allowed us to study novel collisions and ultracold chemical reactions without an apparent reaction barrier. We have discovered evidences to support a universal loss mechanism when an

exothermic reaction channel is available for two molecules that approach sufficiently close to each other. Remarkably, we find that chemical reactions at ultralow temperatures can be controlled by weak long-range interactions where quantum statistics, single scattering partial waves, and quantum threshold laws play dominant roles. In addition, by studying the dependence of the molecular collision dynamics on an applied DC electric field, we can systematically explore the role of dipolar interaction in controlling the reaction rate and also its influence on purely elastic collisions. These experimental results have deepened our understandings on the use of external fields to exert control of dipolar interactions. It has also made clear what future directions we should take to further enhance the phase space density of the dipolar gas.

2. Production of polar molecules in the absolute ground state

We start with a near quantum degenerate gas mixture of fermionic ^{40}K atoms and bosonic ^{87}Rb atoms confined in a crossed-beam far-off-resonance optical dipole trap. Pairs of K and Rb atoms are converted into weakly bound heteronuclear KRb molecules by ramping a DC magnetic field across a Fano–Feshbach resonance. This association process converts ~20% of the atoms into a single weakly bound molecular state. We create 4.5×10^4 heteronuclear Feshbach molecules, with a density of $\sim 10^{12}$ cm^{-3} and an expansion energy of T ~ 300 nK.

The next step is to transfer the weakly bound molecules into their absolute ground state with a fully coherent adiabatic conversion process. Preserving the initial high phase-space density is critical. We use a pair of phase-coherent Raman lasers, separated by a frequency difference of 125 THz and phase stabilized to a common optical frequency comb, to transfer populations adiabatically between the initial and final states. The key is to find an electronically excited intermediate state that has favorable Franck-Condon factors with both the initial and final states. In addition, this intermediate state has mixed singlet–triplet electronic character for coupling predominantly triplet character Feshbach molecules to the singlet rovibrational ground state $X^1\Sigma_0$.

With a two-photon transfer efficiency exceeding 90%, 4×10^4 ground state molecules ($X^1\Sigma_0$, $v = 0$, $N = 0$) are produced. By time-of-flight expansion measurement, we determine the lowest temperature of the ground-state molecules to be 160 nK, a spatial density of 10^{12} cm^{-3}, and a phase space density of 0.06. This dipolar gas is close to quantum degeneracy, with $T/T_F \sim 1.5$. Here T_F is the Fermi temperature.

The properties of the $X^1\Sigma_0$ electronic ground potential, including the rovibrational level structure and the dipole moment, can be measured using the two-photon dark resonance spectroscopy. The dipole moment is determined to be 0.566(17) Debye. In the laboratory frame, the effective dipole moment can be tuned with an external DC electric field. For example, a modest E field of 2 kV/cm results in an effective dipole moment of ~ 0.1 Debye.

We conveniently image these ground state molecules by reversing the two-photon transfer process and putting molecules back to the Feshbach state where we can use resonant probe light to image atomic fluorescence. Recently we have also developed a direct absorption imaging approach for the ground-state molecules. We use a strong optical transition from $X^1\Sigma_0$ $v = 0$ to $1^1\Pi$ $v' = 3$ for the absorption imaging. The advantage of direct absorption detection is that it can work under various external electromagnetic fields and may yield direct evidence for anisotropic properties of the dipolar quantum gas. Once we characterize the detection signal-to-noise ratio, we plan to use this approach as our primary detection tool.

With the KRb molecules prepared in the ground rovibrational level, we turn our attention to the nuclear degrees of freedom [12, 13]. A total of 36 hyperfine states exist, arising from the nuclear spins of Rb ($I_{Rb} = 3/2$) and K ($I_K = 4$). The nuclear spin-spin interaction energy is on the order of a few kHz, comparable to the thermal energy of our ultracold molecules (a few hundred nanoKelvin). However, our experiment is typically performed under a sufficiently large magnetic field where nuclear Zeeman energy is on the order of a few hundred KHz, which is much larger than the molecular thermal energy. Hence it is critical that we prepare the molecules in a single hyperfine state, such as the lowest energy hyperfine state, if we wish to precisely and systematically explore molecular collision and reaction dynamics. Combining the high spectral resolution and the angular momentum selection rules of the coherent optical two-photon transfer process, we can usually prepare the ground-state molecules in a single hyperfine state, but typically not at the lowest one. We then employ a microwave two-photon transition to coherently transfer the population from one hyperfine state to another. Basically, the rotational ground level ($N = 0$) and the first excited level ($N = 1$) are connected by an electric-dipole microwave transition. Within the $N = 1$ manifold, there is a coupling between the rotation and the nuclear quadrupole moment. Hence $N = 1$ can serve as an intermediate level to facilitate a microwave two-photon transition to induce a nuclear spin flip within the $N = 0$ hyperfine manifold. We have demonstrated that we can

prepare the entire molecular sample in a single hyperfine level, and in particular in the lowest energy level.

3. Ultracold chemical reactions

With the molecules prepared in the lowest electronic, rovibrational, and hyperfine energy state, and with the thermal energy significantly lower than any molecular internal energy level separations, one would expect a long lifetime when they are loaded in a far-off-resonance optical dipole trap. Loss due to collisions with the background gas inside the vacuum system and the blackbody radiation-induced excitation of rovibrational transitions both have sufficiently low rates to support a trap lifetime longer than a few tens of seconds. However, we typically observe a trap lifetime of 1 s for a sample density of 10^{12} cm^{-3} and a temperature of 300 nK. The decay of the trapped population can be described well with a two-body loss mechanism, indicating inelastic collisional loss of KRb + KRb even when both are prepared identically in the lowest energy state. With KRb molecules in their lowest possible energy state, KRb + KRb still has possible exothermic reaction channels to form K_2 + Rb_2, K_2Rb + Rb, or Rb_2K + K.

In the ultracold regime, collisions are described by the lowest possible partial waves. For fermionic $^{40}K^{87}Rb$ molecules prepared in an identical quantum state, s-wave contributions are forbidden by the requirement of wave function anti-symmetrization. The lowest possible partial wave is p-wave, which has a centrifugal potential barrier of about 24 μK. Hence, for inelastic collisions to take place at ultralow temperatures, the molecules must tunnel through the centrifugal barrier before a short-range chemical reaction can lead to molecular loss. Experimentally we measure the inelastic loss rate coefficient as a function of the translational temperature of the molecular gas and find that the rate coefficient is linearly proportional to temperature and approaches zero as temperature drops. This temperature dependence can be described exactly by the Wigner threshold law for the p-wave collisions. Further, the magnitude of the rate coefficient agrees well with predictions from a universal loss model [14]. In this model, once two molecules approach each other sufficiently close, such as behind the p-wave barrier, they have a near unity probability of loss due to short-range reactions. Hence, the predicted loss rate coefficient can be analytically derived and it depends only on the combined potential formed by the inter-molecular van der Waals interaction and the p-wave centrifugal barrier.

The universal loss picture becomes further simplified if we remove the centrifugal barrier by permitting s-wave collisions. This can be accomplished by

 preparing the KRb molecules in two different nuclear spin states within the rotational ground level. In this case the universal loss can be predicted based on a purely long-range parameter associated with the van der Waals potential, namely the van der Waals length. The experimental measurements show a loss rate coefficient that is temperature independent and is generally one or two orders of magnitude higher than the previous case with p-wave. Experiment-theory agreement is again good.

This s-wave collision experiment can also be performed between an atom and a molecule. When an ultracold K atom and a KRb molecules collide, with both prepared in their absolute lowest energy states, we observe a loss rate coefficient that is similar to that of the s-wave molecular collision. On the other hand, for KRb and Rb, with all experimental conditions prepared in the same way as for KRb + K, the observed loss rate coefficient is suppressed by at least an order of magnitude. This supports the prediction that KRb + K $\rightarrow$ K_2 + Rb is exothermic and thus allowed, whereas KRb + Rb $\rightarrow$ Rb_2 + K is endothermic and thus forbidden.

These experimental observations provide conclusive evidence for barrier-less chemical reactions taking place at ultralow temperatures. The reaction rate can be fully determined by simple long-range potentials, quantum statistics, and threshold laws. This opens the possibility for precise, quantum-state control of chemical reaction processes.

4. Dipolar collisions with inelastic and elastic contributions

In the absence of an electric field, the effective molecular dipole moment in the laboratory frame is zero and the collision process is described by angular momentum partial waves. When an external electric field is applied and the molecules are polarized, this situation changes drastically. One can think of this scenario as a breakdown of the partial wave picture since the dipole-dipole interaction does not have a spherical symmetry, and thus different partial waves can get mixed together. Alternatively, as the dipole moment becomes gradually stronger with an increasing E-field, we can still use the framework of partial waves but need to add increasingly important anisotropic interactions to describe the collision process. For example, as schematically shown in Fig. 1, different components of the p-wave collision experience different barrier heights. As we enhance the effective dipole moment with an increasing E, the inelastic collision loss rate, as discussed in the previous section, will be increasingly dominated by the $m_l = 0$ channel, whereas the contributions from the $m_l = \pm 1$ components will be reduced and eventually become negligible. At a

sufficiently strong value of E, we can thus model the inter-molecular potential as the sum of the centrifugal barrier, the van der Waals interaction, and an attractive dipolar interaction. The last term can be sufficiently strong to completely overcome the original centrifugal barrier, making the collision process barrier-less.
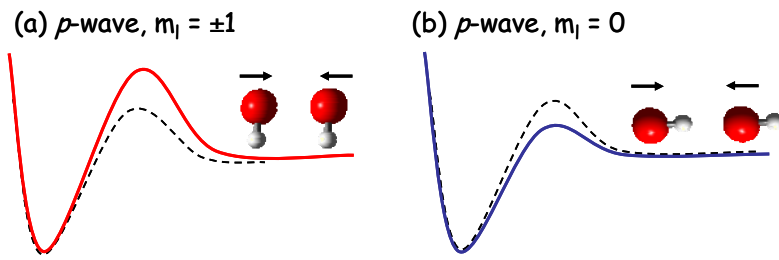

(a) p-wave, $m_l = \pm 1$ **(b)** p-wave, $m_l = 0$

Figure 1 Collisions between two fermionic dipolar molecules. The dashed line represents the centrifugal barrier of the p-wave collision in the absence of an external electric field, namely, when the molecules are unpolarized. When an external electric field is applied, the $m_l = \pm 1$ component of the p-wave collision faces an increased barrier height due to dipolar repulsion, as shown in (a). On the other hand, the $m_l = 0$ component experiences a reduced barrier height as the two dipole attract each other.

Experimentally we have observed a strong dependence of the inelastic molecular two-body loss rate on the effective dipole moment. At a sufficiently weak E-field, the loss can be modeled quantitatively with the van der Waals potential plus the centrifugal barrier, as discussed in the previous section. When the effective dipole moment (d_{eff}) reaches beyond 0.1 Debye, the attractive dipolar interaction starts to play an important role and the collisional barrier continues to decrease, leading to a rise of the loss rate coefficient as a function of d_{eff}^{6}. The heating of the gas sample resulting from this inelastic loss process can also be quantitatively modeled.

The elastic cross section for dipolar collisions is predicted to scale as d_{eff}^{4} [15]. To evaporatively cool the molecules to lower temperatures, the elastic collision rates must dominate over the inelastic rates. In an anisotropic optical trap, we can create a temperature difference between two orthogonal directions and monitor the rate of gas thermlization as a means to measure the elastic collision rates. However, in the current experiment, as we increase d_{eff}, we experience a strong increase of anisotropic inelastic loss, which can mask the role of elastic collisions. It is clear that evaporation in the three dimensional optical trap is not promising.

5. Scientific Outlook

The successful production of high phase-space density ultracold polar molecules has allowed us to explore dipolar collisions at ultralow temperatures. As we gain a good understanding of dipolar collisions in a three dimensional space, it has become clear that we need to take advantage of a reduced trap geometry, in addition to the external fields that we apply, to further refine our control of molecular collisions. For example, a two-dimensional optical trap can be used to effectively eliminate the inelastic $m_l = 0$ loss channel from the p-wave collision [16]. The remaining strong elastic collisions will then allow efficient evaporative cooling of molecules to take place. Once reaching quantum degeneracy, novel strongly correlated system dynamics can be explored with various dipole trap and optical lattice geometries. We can start to explore an exciting range of scientific topics including quantum phase transitions, quantum information processing, precision measurement, and novel collisions and chemical reactions at ultralow energies. We are excited that a qualitatively new field is being opened.

Acknowledgments

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