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Dissociation and Decay of Ultracold Sodium Molecules

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The dissociation of ultracold molecules was studied by ramping an external magnetic field through a Feshbach resonance. The observed dissociation energies directly yielded the strength of the atom-molecule coupling. They showed nonlinear dependence on the ramp speed. This was explained by a Wigner threshold law which predicts that the decay rate of the molecules above threshold increases with the density of states. In addition, inelastic molecule-molecule and molecule-atom collisions were characterized.

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Recently, it has become possible to create ultracold molecular gases from precooled atomic samples [1–11]. Extending the ultralow temperature regime from atoms to molecules is an important step towards controlling the motion of more complicated objects. The complex structure of molecules may lead to new scientific opportunities, including the search for a permanent electric dipole moment, with sensitivity much higher than for heavy atoms [12], and the realization of quantum fluids of bosons and fermions with anisotropic interactions [13]. Furthermore, stable mixtures of atomic and molecular condensates are predicted to show coherent stimulation of atom-molecule or molecule-atom conversion, constituting quantum-coherent chemistry [14].

To date, all realizations of ultracold molecules (< 1 mK) have bypassed the need for direct cooling of the molecules, which is difficult due to the complicated rovibrational structure. Rather, molecules were formed from ultracold atoms using Feshbach resonances [2–11], where a highly vibrational excited molecular state is magnetically tuned into resonance with a pair of colliding atoms.

In this Letter, we study the dissociation and decay of such highly excited molecules. Figure 1 shows a schematic of the dissociation process. For magnetic fields above the Feshbach resonance, the molecular state crosses the free atomic states, shown here as discrete states in a finite quantization volume. The interaction between atoms and molecules turns these crossing into anticrossings. When the magnetic field is swept very slowly through the resonance, the molecules follow the adiabatic curve and end up in the lowest energy state of the atoms. For faster ramps, the molecular populations will partially cross some of the low-lying states, and the dissociation products will populate several atomic states. The stronger the coupling between the molecular state and the atomic states, the faster the molecules dissociate and the smaller the energy release in the dissociation. Observing the atom-molecule coupling in *one-body* decay (dissociation) is a new method to experimentally determine the strength of a Feshbach resonance. Previous measurements used *two-* or *three-body* processes to characterize the Feshbach resonance and therefore required accurate knowledge of the atomic density distribution.

Collisional properties of the molecules were also studied. Inelastic collisions limit both the production of molecules and their lifetime. We observed loss of molecules by collisions both with atoms and other molecules. These two processes were studied by separating atoms and molecules with a short pulse of laser light [9].

To generate molecules, sodium condensates in the $|F, m_F\rangle = |1, -1\rangle$ state were prepared in an optical dipole trap. The trap frequencies of 290 Hz in the radial direction and 2.2 Hz in the axial direction yielded typical densities of 1.7×10^{14} cm^{-3} for 5×10^6 atoms. Atoms were then spin-flipped using an adiabatic radio frequency sweep to the $|1, 1\rangle$ state, where a 1 G wide Feshbach resonance exists at 907 G [15].

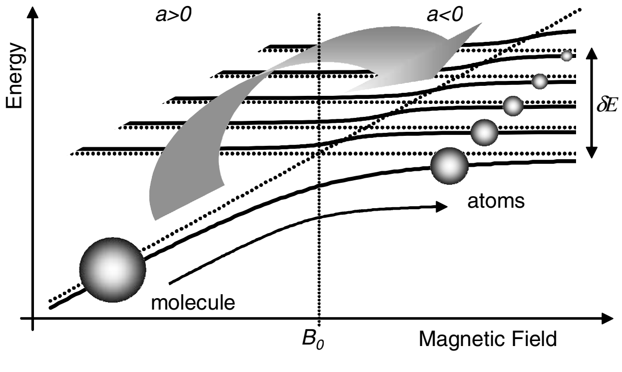

FIG. 1. Schematic diagram of energy levels for molecules and atoms. The diabatic energy levels are shown as dashed lines. The adiabatic curves (solid lines) include the atom-molecule coupling. When the magnetic field is swept from positive to negative scattering length, dissociated molecules end up in one or several atomic states, depending on the ramp rate of the magnetic field. The spheres represent the distribution of the population before and after the ramp.

The magnetic field sequence used to create and detect Na_2 molecules was identical to our previous work [9]. Briefly, the axial magnetic field was ramped to 903 G in 100 ms using two pairs of bias coils. In order to prepare the condensate on the negative scattering length side of the resonance, the field was stepped up to 913 G as quickly as possible (~ 1 μs) to jump through the resonance with minimal atom loss. The field was then ramped back down to 903 G in 50 μs to form molecules. In order to remove nonpaired atoms from the trap, the sample was irradiated with a 20 μs pulse of resonant light. Because 903 G is far from the Feshbach resonance, the mixing between atomic and molecular states was small and therefore molecules were transparent to this "blast" pulse. By ramping the field back to 913 G molecules were converted back to atoms. Absorption images were taken at high fields (either at 903 or 913 G) after 10 to 17 ms ballistic expansion, with the imaging light incident along the axial direction of the condensate.

To study the momentum distribution of the back-converted atoms, the magnetic field was ramped up immediately after turning off the optical trap, or for a reference, at the end of the ballistic expansion. The difference between the energies of ballistic expansion is the released dissociation energy. Energies were obtained from the rms width of the cloud $\langle x^2 \rangle$ as $E = 3m\langle x^2 \rangle / 2t^2$, where t is the ballistic expansion time and m is the atomic mass. Figure 2 shows that faster field ramps created hotter atoms.

An earlier theoretical treatment assumes a constant predissociation lifetime of the molecules and predicts a linear relation between dissociation energy and field ramp rate [16]. This theory predicts a much faster dissociation (and therefore smaller dissociation energy) than was observed. Furthermore, our data show a nonlinear dependence. Linear behavior would be expected if the lifetime of the molecules was independent of the energy ϵ from the dissociation threshold. The fact that the slope becomes smaller for increasing ramp rate indicates that the lifetime of molecules decreases with the ramp rate. As we show, this can be explained by an increase of the density of atomic states, leading to a $\sqrt{\epsilon}$ dependence of the molecular decay rate (Wigner threshold law [17]).

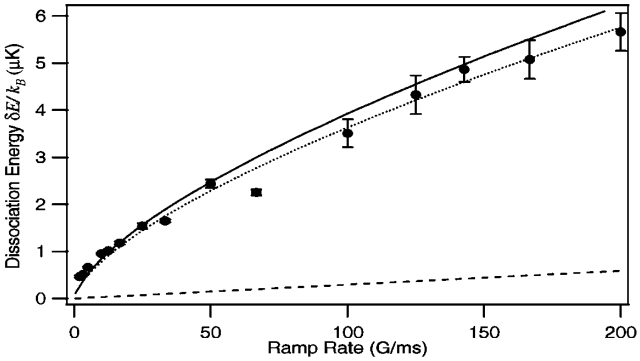

FIG. 2. Dissociation energy of molecules as a function of magnetic field ramp rate. The dashed line represents the linear relation described in Ref. [16], the solid line shows the result of our model using a theoretical value for $\Delta B = 0.98$ G and $a_{\mathrm{bg}} = 3.4$ nm, and the dotted line shows a curve with the product $a_{\mathrm{bg}}\Delta B$ as a fitting parameter.

The decay rate $\Gamma(\epsilon)$ follows from Fermi's golden rule as $\hbar\Gamma(\epsilon) = 2\pi|V_{\mathrm{ma}}(\epsilon)|^2 D(\epsilon)$ [18], where V_{ma} is the matrix element between atomic and molecular states, which to leading order is independent of ϵ. The density of states $D(\epsilon)$ is given by

$$D(\epsilon) = \frac{V}{(2\pi)^2}\left(\frac{m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}, \tag{1}$$

where V is the quantization volume for free atomic states.

An expression for the matrix element V_{ma} is obtained by comparing the energy shift near a Feshbach resonance with second-order perturbation theory. Assuming two atoms in a volume V, the energy shift of the low-lying continuum states due to the coupling with a bound molecular state is

$$\delta(\epsilon) = \frac{|V_{\mathrm{ma}}|^2}{\epsilon} = \frac{|V_{\mathrm{ma}}|^2}{\Delta\mu(B - B_0)}, \tag{2}$$

where $\Delta\mu$ is the difference between atomic and molecular magnetic moments, B is the applied magnetic field, and B_0 is the position of the Feshbach resonance.

The energy shift can also be expressed in terms of the mean field energy $4\pi\hbar^2 a/mV$, where $a = a_{\mathrm{bg}}\Delta B/(B - B_0)$ is the scattering length near the Feshbach resonance (a_{bg} is the background scattering length and ΔB is the resonance width [19]):

$$\delta(\epsilon) = \frac{4\pi\hbar^2}{mV}\frac{a_{\mathrm{bg}}\Delta B}{B - B_0}. \tag{3}$$

Comparing Eqs. (2) and (3) yields

$$|V_{\mathrm{ma}}|^2 = \frac{4\pi\hbar^2}{mV} a_{\mathrm{bg}}\Delta\mu\Delta B. \tag{4}$$

If the entire population is initially in the molecular state, the fraction of molecules, $m(\epsilon)$, at energy ϵ follows the rate equation,

$$\frac{dm(\epsilon)}{d\epsilon} = \frac{dm(\epsilon)}{dt}\left(\frac{d\epsilon}{dt}\right)^{-1} = \Gamma(\epsilon)m(\epsilon)\left(\frac{d\epsilon}{dt}\right)^{-1} \tag{5}$$

$$= \frac{2\pi|V_{\mathrm{ma}}(\epsilon)|^2 D(\epsilon)}{\hbar\Delta\mu|\dot{B}|}m(\epsilon). \tag{6}$$

Using Eqs. (1) and (4), we solve the differential equation for $m(\epsilon)$,

$$m(\epsilon) = e^{-(2/3)C\epsilon^{3/2}}, \qquad C = \frac{2\Delta B}{\hbar\dot{B}}\sqrt{\frac{ma_{\mathrm{bg}}^2}{\hbar^2}}. \tag{7}$$

In the laboratory frame, the atoms have kinetic energy $\epsilon/2$, and therefore the average energy of an atom after dissociation is

$$\delta E = \int_0^\infty \frac{\epsilon}{2}[-dm(\epsilon)] = 0.591\left(\sqrt{\frac{\hbar^2}{ma_{\rm bg}^2}}\frac{\hbar\dot{B}}{2\Delta B}\right)^{2/3}. \qquad (8)$$

Using theoretical values $a_{\rm bg} = 3.4$ nm, $\Delta\mu/h = 3.65 \times 1.4$ MHz/G, and $\Delta B = 0.98$ G [20,21], the data show good agreement with our model. A fit of the product $a_{\rm bg}\Delta B$ to our data results in $a_{\rm bg}\Delta B = 3.64$ G nm $\pm$ 2% (dotted line in Fig. 2). The discrepancy between the theoretical and fitted values is 4 times bigger than the statistical error, but within the systematic error of the measurement of the release energy.

Further experiments with ultracold sodium molecules will critically depend on their collision properties. Therefore we also studied heating and inelastic collision processes. As shown in Fig. 3, we observed monotonic heating of the pure molecular sample over ~30 ms. In addition, we observed short time scale oscillations (6 ms) in the fitted temperature (inset of Fig. 3). Such breathing oscillations were excited because the molecules were formed over the volume of the atomic condensate and started oscillations around their equilibrium volume. The equilibrium volume deduced from the observed released energy is much smaller than the initial volume. The absence of damping implies a collision time of at least 6 ms, or a molecular scattering length smaller than 17 nm (obtained using the expression for the collision rate $8\pi a^2 v_{\rm th} n_m$, where $v_{\rm th}$ is the thermal velocity). It is unclear whether the oscillation disappeared due to collisions or limited signal-to-noise ratio.

The temperature of the molecular cloud saturated at ~250 nK after 15 ms. A possible explanation is the balance between heating due to inelastic molecular decay and the evaporative cooling caused by the finite trap depth (1.7 μK). This would imply a collision time of 15 ms. However, we have no clear evidence that thermalization has occurred. Clearly, further studies of elastic collisions between ultracold molecules are necessary.

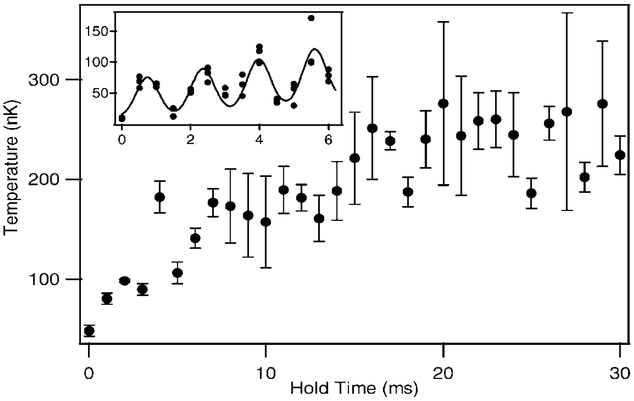

FIG. 3. Temperature of the molecular cloud. After 15 ms, the temperature saturates at ~250 nK. Error bars represent the statistical error (standard deviation). The inset shows finer resolution data for holding times up to 6 ms. The solid line is a guide to the eye.

Molecules formed via an s-wave Feshbach resonance are created in the rotational ground state, but in high vibrational states. Therefore, one expects vibrational relaxation to be a strong, inelastic decay mechanism.

Figure 4(a) shows the decay of a pure molecular sample. The decay was analyzed with the rate equation

$$\frac{\dot{N}_m}{N_m} = -K_{mm} n_m. \qquad (9)$$

Here N_m, n_m is the number and the density of the molecules, respectively, and K_{mm} is the molecule-molecule collision rate coefficient. Because of the changing size and temperature of the molecular cloud during the first ~15 ms (Fig. 3), we fit data points only at later times, assuming a thermal equilibrium volume for the molecules. The decay at earlier times is slower, consistent with a larger molecular cloud. The fit yields a molecule-molecule collision coefficient of $K_{mm} \sim 5.1 \times 10^{-11}$ cm^3/s, about 2 orders of magnitude larger than the typical values reported for fermions [4,5].

Inelastic collisions between molecules and atoms were also observed by keeping atoms in the trap [Fig. 4(b)]. The decay was analyzed assuming that the loss of

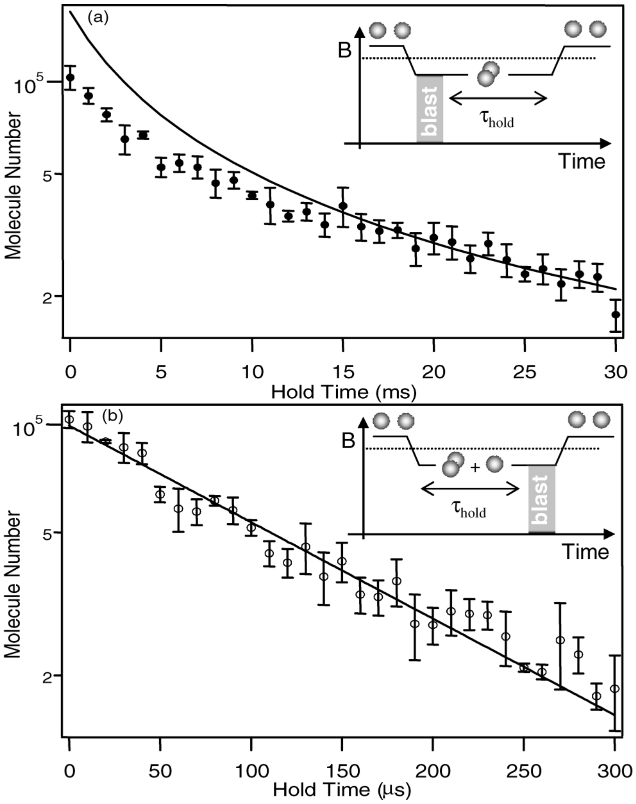

FIG. 4. Decay of ultracold molecules trapped alone (a) or together with atoms (b). The solid lines in (a) and (b) are fits of Eqs. (9) and (10) to data, which assume vibrational relaxation in the collision of m olecules (a) or collisions between molecules and atoms (b). The insets illustrate the experimental sequences.

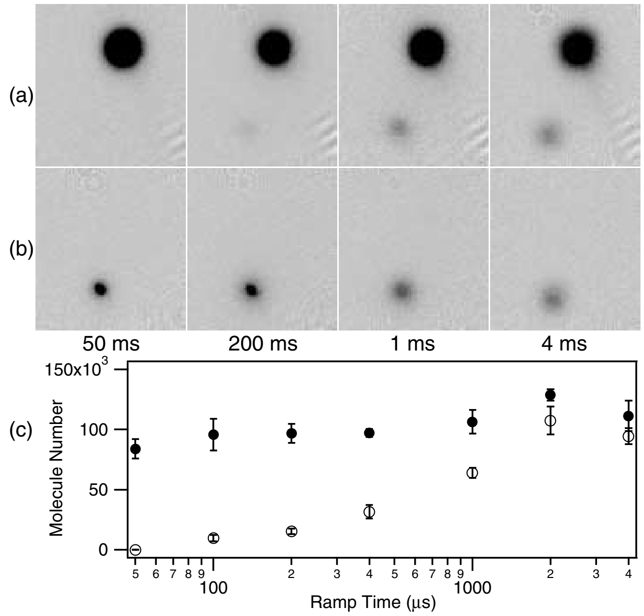

FIG. 5. Conversion of atoms to molecules for various ramp times. During a given time, the magnetic field was swept by 10 G. (a) and (b) show absorption images taken after 14 ms time of flight. The molecules (bottom) were radially separated from the atoms (top) by a field gradient of 2.8 G/cm. The molecules were converted back to atoms only 0.5 ms before imaging by ramping the magnetic field back across the Feshbach resonance. This time was chosen to be long enough for any transient field fluctuations to damp out, but short enough such that the size of the imaged cloud reflected the molecular temperature, not the dissociation energy. (a) The atoms remained in the trap. (b) The atoms were removed by a resonant laser pulse immediately after the magnetic field ramp. (c) Number of molecules as a function of ramp time for (a) (open circles) and (b) (closed circles).

molecules occurred mainly due to collisions with atoms, resulting in an exponential decay:

$$\frac{\dot{N}_m}{N_m} = -K_{am} n_a. \tag{10}$$

Here n_a is the density of atoms, and K_{am} is the atom-molecule collision rate coefficient. From the fit, we extract a lifetime of 106 μs and a rate coefficient $K_{am} \sim 5.5 \times 10^{-11}$ cm^3/s, which agrees well with theoretical predictions [21,22].

The inelastic losses determine the maximum conversion efficiency from atoms to molecules. For an adiabatic ramp, one expects close to 100% conversion efficiency. Indeed, in experiments with fermionic atoms, efficiencies up to 85% have been observed [5]. Figure 5 shows the results for magnetic field ramps of different durations. The two sets of images show that applying the blast pulse dramatically improved the molecular number and temperature. Without it, a slower ramp time (4 ms) appeared to be more favorable for molecule formation [open circles in Fig. 5(c)]. No molecules were observed for a 50 μs ramp time. However, with the blast pulse, a similar number of molecules was obtained for all ramp times between 50 μs to 4 ms [closed circles in Fig. 5(c)].

We assume that these results reflect the interplay of two competing processes. The adiabatic condition requires a relatively slow field ramp for efficient conversion. However, this means that the atoms and molecules spend more time near or at the Feshbach resonance, where inelastic collision rates are enhanced. In contrast to Fig. 5(b), the absence of a molecular signal in Fig. 5(a) for 50 μs ramp time reflects that the atomic density reduction due to the ballistic expansion is too slow for the molecules to survive the inelastic collisions with the atoms.

In conclusion, we observed a Wigner threshold behavior in the dissociation of ultracold molecules. We were able to characterize a Feshbach resonance using a one-body decay (dissociation) process. The rapid decay of the molecules due to collisions with atoms and other molecules imposes a severe limit to further evaporative cooling for bosons. This also explains the low conversion efficiency ($\sim 4\%$), in contrast to recent experiments with fermions.

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