Laser Modification of Ultracold Collisions: Experiment

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Julienne recently predicted a dramatic laser-intensity-dependent modification of the associative ionization (AI) rate in ultracold collisions. We observe such a modification, but with a behavior inconsistent with the originally proposed mechanism. Furthermore, we find resonant structure in the spectrum of AI rate versus laser frequency, showing the importance of molecular bound states in the AI process. These observations are explained in a new theoretical treatment by Julienne and Heather (preceding Letter).

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Laser cooling and trapping techniques have recently allowed a number of atomic collision experiments [1–4] at temperatures ≤ 1 mK. The nature of collisions in this energy regime is quite different from that at higher energies. For example, light shifts due to high-intensity laser fields can be much larger than the thermal energies and can substantially alter the collision dynamics. The duration of these ultracold collisions can become much longer than most excited-state lifetimes as well. This reversal of the usual situation means that spontaneous emission will play a new role in excited-state collisions [5–11].

In a series of experiments, we have studied the associative ionization (AI) reaction in ultracold sodium in a laser trap [2,3]:

$$\mathrm{Na}+\mathrm{Na}+2h\nu \rightarrow \cdots \rightarrow \mathrm{Na}_2^{+}+e^{-}.$$

At higher collision energies the reaction can be considered as the collision of two Na atoms that have been resonantly excited by the photons. Our measurements demonstrate that this simple picture is insufficient at ultracold temperatures and emphasize the unique nature of ultracold collisions.

Theoretical studies of AI at ultracold temperatures predict a strong dependence on the light intensity [5]. More precisely, a change in the laser intensity will have a profound effect on the reaction rate over and above the change caused by simple laser-induced alteration of the concentration of the excited "reactants." This is a new class of laser-controlled chemical reactions distinct from the usual cases in which the laser simply prepares reactants in specific states.

Here we report a measurement of this laser modification of AI by the time-varying light fields in our laser trap. Our observations show a large increase in the ionization rate during the high-intensity ("trapping") periods of our trap when compared to the low-intensity ("cooling") periods. The modulation qualitatively supports an earlier prediction by Julienne [5]. Quantitatively, however, it is in disagreement. This early estimate was based on an understanding of AI as a collision of excited-state [Na(3P)+Na(3P)], two-level atoms prepared at large internuclear separation. The ratio of the ionization rates measured under high- and low-laser-intensity conditions was estimated [5] to be $\sim 10^4$. The measurements presented here indicate a ratio of $\sim 10^2$.

The original prediction was based on the following considerations: Two atoms approach and, at long range, are unaffected by each other but are strongly affected by the laser field. The most appropriate picture is then of individual atoms interacting with the laser field (field-dressed states). As they approach, the atom-atom interaction grows and detunes the atoms so that, at some field-strength-dependent distance, the atoms will decouple from the field. The uncoupled "quasimolecule" must survive in a doubly excited state while it moves to the small internuclear separation where AI can occur. At low laser intensity and small detuning the decoupling occurs at a large distance and such survival is unlikely. At high intensity the decoupling occurs at smaller distances and, in addition, the atoms are accelerated by their interatomic potential to velocities much higher than their very low initial velocities. Both of these factors favor survival of the excited $P+P$ complex and increase the AI rate. The results presented below have prompted a change in this theoretical view.

Our laser trap is a two-focus trap using both the spontaneous and dipole light-pressure forces for confinement. The trap, described in more detail elsewhere [2,3], is sketched in Fig. 1: Two counterpropagating laser beams

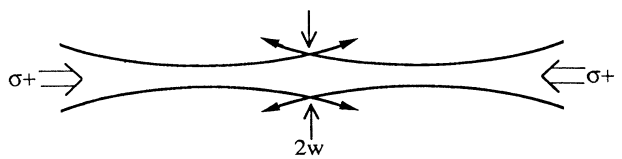

FIG. 1. Sketch of the trap geometry (not to scale). Foci of the two beams are separated by about the confocal parameter. Stable trapping is achieved at the midpoint between the foci where the waist ($1/e^2$ radius of intensity) is w.

are brought to separate foci in a region of optical molasses. Radial confinement is provided by the dipole-force potential in the tightly focused beams, which are tuned below resonance; the longitudinal trapping force is provided by radiation pressure, which is balanced halfway between the two foci. The beams are circularly polarized to take advantage of the largest matrix element for the optical transition. The trap beams are alternated in time to avoid standing-wave heating effects and these trapping periods are further alternated with periods when neither trap beam is on. This allows the molasses beams to provide damping. The molasses beams are on continuously, but the large ac Stark shifts, present for atoms in the trap region while either trap beam is on, effectively detune those atoms so that essentially no damping can take place in the trap region during these intervals.

The four periods of a trapping cycle are of equal duration, several microseconds long, during which time the atoms can move only a few micrometers. The power in each trap beam is ~ 40 mW. The foci, each of approximately 100-μm $1/e^2$ radius, are separated by about one confocal parameter (~ 5 cm), so the intensity at the center of the trap is 2.0×10^5 mW/cm^2. The trap laser, unless otherwise noted, was detuned by $\Delta_{\text{trap}} \approx -600$ MHz from the Na $(3S_{1/2}, F=2) \rightarrow (3P_{3/2}, F'=3)$ transition at 589 nm (linewidth $\Gamma = 2\pi \times 10$ MHz). This gives a time-averaged radial well depth of about 10 mK. The six molasses beams each have an intensity of ~ 8 mW/cm^2 in the trap region and are typically detuned by $\Delta_{\text{molasses}} \approx -10$ MHz from the resonance. Approximately 20% of this power is in a pair of sidebands 1.7 GHz from the carrier, one of which serves to repump any atoms that decay to the $F=1$ ground state during the molasses cooling periods. The confinement volume is small, $\sim 10^{-6}$ cm^3, but densities of 10^{10}-10^{11} cm^{-3} can yield ion count rates of ~ 1 kHz. The density does not change by more than 20% peak to peak as the trap is cycled.

Previous measurements [2] have indicated that the mean kinetic energy of atoms in the trap corresponds to a temperature of approximately 0.75 mK. This value is significantly higher than the cooling limit in the molasses alone [12] because of additional heating and reduced cooling due to the large ac Stark shifts in the trap region.

Ions formed in the trap are accelerated into a focused-mesh electron multiplier and counted. The pulses are fed into a signal averager synchronized to the trap periods, and accumulated over many cycles. Typical ion signals are shown in Figs. 2(a) and 2(c). Fluorescence from the trap, on the $3P$-$3S$ transition, is imaged onto a photomultiplier and this is similarly recorded [Figs. 2(b) and 2(d)]. Such measurements are repeated with the trapping laser blocked to serve as a background measurement, which has been subtracted from the signals of Fig. 2. Figures 2(a) and 2(c) clearly show a strong modulation in the ion signal that is correlated with the trap

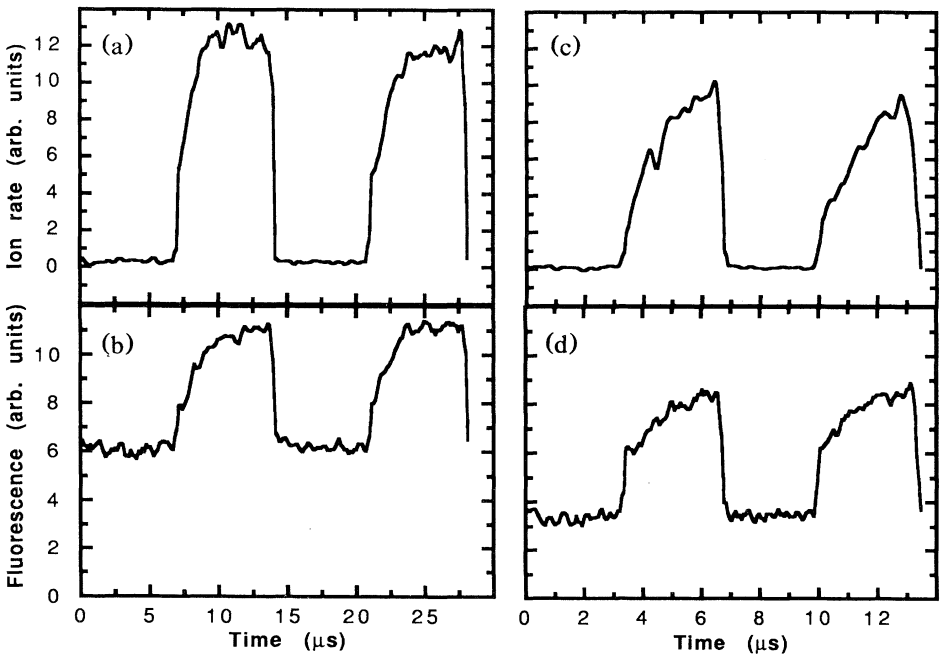

FIG. 2. (a) Ion signal vs time for $\Delta_{\text{molasses}} = -8.5$ MHz, and cycle periods of 7.14 μs. (b) Fluorescence vs time for the same conditions as (a). (c) Ion signal vs time for $\Delta_{\text{molasses}} = -15$ MHz, and cycle periods of 3.33 μs. (d) Fluorescence vs time for the same conditions as (c). The time-of-flight of the ions to the detector has been taken out to align the fluorescence and ion signals from the same trap or cooling phase. The trap laser is on during the periods of larger ion or fluorescence signal. The vertical scales in (a) and (c) and in (b) and (d), although arbitrary, are kept the same.

phases.

The theoretical estimate in the preceding Letter [13] of the trap-cycle AI rate is made assuming that the atoms are optically pumped into the stretched ($m_F = F_{max}$) states by the circularly polarized trap beams. In the experiment the cooling phase distributes the population among the magnetic sublevels, whereas the circular polarization of the trap laser pumps the atoms back into the stretched state. Relying on power broadening rather than frequency sidebands to recover atoms that fall into the $F=1$ ground state during the trap periods, this process takes several microseconds. This is believed to account for the initial slope in the fluorescence during the trapping periods [Figs. 2(b) and 2(d)]: the fluorescence increasing slowly as the atoms are pumped onto the strongest, cycling, transition. Thus, a determination of the AI rate for stretched-state atoms in the trap is made only after the atoms have had sufficient time to optically pump over into this state.

A measure of the different nature of AI in high and low intensity is obtained by taking the ratio of the detected ion rates in the trapping and cooling phases. For the conditions of Fig. 2(a), with $P_{trap}=44$ mW, $\Delta_{trap}=-0.6$ GHz, $I_{molasses}=8$ mW/cm^2 per beam, $\Delta_{molasses}=-8.5$ MHz, and cycling periods of 7 μs, the ratio of the high- to low-intensity rate is 41^{+21}_{-7}. For the conditions of Fig. 2(c), (where $\Delta_{molasses}=-15$ MHz, and cycling periods are 3.3 μs), this ratio is 100^{+120}_{-40}. Uncertainties are estimated from the scatter in the measurements. Ratios in the range of 20 to 200 have been recorded under varying conditions, with most observations falling between 40 and 100. Some of the variations in the measured ratio are due to dependences on such parameters as molasses-laser detuning, the laser intensities, and the length of the trapping periods; however, the large uncertainty in our data does not allow us to make any conclusive statements about these variations. The ratio is about 2 orders of magnitude smaller than the original prediction [5], which assumed adiabatic following from a field-dressed entrance channel that is predominately $P+P$ at large separation.

Figure 3 shows the spectrum of the integrated ion signal versus the trap-laser detuning. This spectrum is also not explained by the original picture. In that picture the

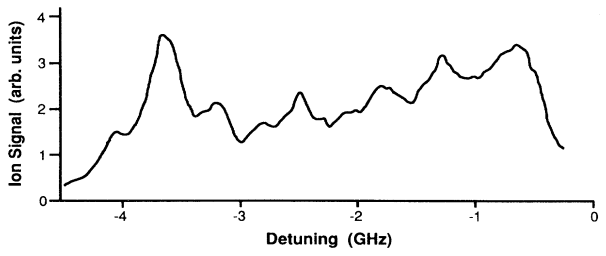

FIG. 3. Integrated ion signal vs trap-laser detuning for $\Delta_{molasses}=-8.5$ MHz.

population of the predominantly $P+P$ field-dressed atomic entrance-channel states that lead to AI is a rapidly and monotonically decreasing function of laser detuning. By detuning the trap from $\Delta_{trap}\sim-0.6$ GHz to ~-4.0 GHz the flux in this entrance channel will be reduced by 4 orders of magnitude. The fact that we are still able to observe an ion signal at all with relatively large detunings implies that the asymptotically $P+P$ AI channel cannot be dominant. Time-resolved measurements for large trap detunings show a modulation in the ion signal quantitatively similar to that seen in Fig. 2. The fluorescence modulation and hence the excited-state population, on the other hand, flattens out and reverses: For large detunings the fluorescence during the trap periods is less than during the molasses periods.

The presence of relatively narrow resonance features in the AI spectrum in Fig. 3 leads one to consider AI pathways with intermediate molecular states that can provide these resonant structures. Although these pathways contribute insignificantly to AI at large collision energies, they are believed to be essential to the dominant excitation paths leading to AI at these low energies. These new pathways for AI are primarily of ground-state ($S+S$) character at long range [13]. In both trapping and molasses phases the same Na_2 doubly excited 1_u state (asymptotically $P+P$) must be excited via an intrinsically molecular, two-step mechanism. In the trap phase, when detuning is large, molecular bound-state resonances on intermediate potentials (asymptotically $S+P$) lead to excitation of the doubly excited 1_u state at the relatively small internuclear separation $R\approx 60a_0$. By contrast, the small detuning in the molasses phase results in both of these excitations occurring at very large internuclear separation, $\geq 1000a_0$, and excited-state decay while moving to small R leads to a decreased AI rate. In both the high- and low-intensity cases the final molecular state preceding ionization is the doubly excited 1_u state, so that the ratio of rates discussed above is insensitive to the specific value of the ionization probability from this state, but is strongly affected by the excitation and survival process. The value of this ratio estimated by Julienne and Heather is consistent with our measurements [13].

Now consider the rate coefficient K_{AI}. Traditionally, one would write the rate of ionization per unit volume as $R=K_{AI}n_r^2$, where n_r is the density of reacting atoms. The forgoing discussion concerning the new view of AI [13] shows that no simple identification of the reactants, such as excited atoms, is possible. We define an effective rate coefficient with the reactants being Na atoms, regardless of state. Using the rate coefficient [14] and excited-state fraction [14] of Ref. [2], and the ratios measured here, we calculate effective rate coefficients for AI of $(2.6^{+3.0}_{-1.2})\times10^{-12}$ cm^3/s for high intensity and $(4.3^{+5.5}_{-2.6})\times10^{-14}$ cm^3/s for low intensity. These values are in reasonable agreement with those given by Julienne and Heather [13].

The intermediate states in the analysis of Ref. [13] are the "pure long-range states" of the Na_2 molecule predicted by Stwalley, Uang, and Pichler [15]. These states have inner turning points at larger distances than where most bound states have their outer turning points. Although these states were predicted some time ago, they have proven extremely difficult to create or observe. Perhaps ultracold collision experiments will provide a means of studying them in the future.

Interpretation of the structure in Fig. 3 is complicated by the fact that the temperature of the atoms and the shape and depth of the trap potential also change as the trap laser is detuned. These are expected to vary smoothly, however, with the temperature decreasing and the trap potential weakening monotonically as the detuning gets large. The structure that is apparent in Fig. 3 is on too fine a scale to be due to this type of variation. Additionally, simultaneous measurements of the trap fluorescence display no such features, as might be expected if the "resonances" were due to changes in the density or distribution of atoms. There is some variation in the envelope of the peak heights related to molasses-laser tuning and trap alignment, but the existence and location of the peaks do not vary.

In order to clearly identify the intermediate states involved in the ultracold AI reaction we wish to perform "two-color" experiments in which one can leave the trap-laser frequency fixed while varying the frequency of an additional probe laser. This will enable the separate excitation of the singly and doubly excited Na_2 intermediates and allow for much simpler and more positive identification of the states. This configuration has the additional feature of maintaining the trap conditions (temperature, density, etc.) fixed while scanning the frequency of the additional laser, allowing some information about transition strengths to be extracted as well. We have performed some preliminary experiments that indicate that much more interesting resonant structure is available to be explored at frequencies well beyond the $\sim$4-GHz range that we were limited to here (where the trap laser needs to be tuned for strong enough trapping to produce a good ion signal).

In conclusion, we have seen a change of the AI reaction rate coefficient, by a factor of $\sim$60, that we believe is due to laser-intensity modification of the reaction dynamics at ultracold temperatures. In addition, we have made frequency-dependent measurements of the AI rate which exhibit resonant structure. These new measurements have revealed shortcomings in the previous understanding of the AI reaction. The new theory of Julienne and Heather [13] is able to account for the distinctive features of these measurements by including the effects of intermediate long-range molecular states and the effects of the large, laser-induced light shifts present in the experiment.

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