Final Report: DE-FG02-92ER14263

Experiments in Ultracold Molecules

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Since this grant covered a 24-year period, from 5/1/92 – 3/31/16 (plus a one-year no-cost extension), the focus of the research evolved significantly during that time. The initial interest was in studying ultracold collisions which occurred in laser traps. This evolved into *controlling* these collisions, eventually leading into *coherent* control of the collisions with frequency-chirped light. The emphasis then switched into the area of ultracold molecules, specifically the production of these molecules by a specific type of ultracold collision: photoassociation. This laser-induced molecule formation was done with frequency-chirped light, maintaining the theme of coherent control on nanosecond time scales. This final report is divided into sections corresponding to the three-year grant periods.

5/1/92-4/30/95 Progress Report:

We devoted significant effort toward understanding our magneto-optical laser trap. The collisions we are studying involve atoms confined in this trap, and it is important to understand the conditions under which these ultracold collisions take place. Some of our recent work investigated how the rate of trap-loss collisions depends on trap laser intensity. Our results displayed an interesting isotopic (^{85}Rb vs. ^{87}Rb) difference in this dependence, leading us to conclude that hyperfine-state changing collisions dominate at low trap intensities while collisions between a ground-state atom and an excited-state atom (most likely a fine-structure changing collision) dominate at higher trap intensities. However, as we vary the trap laser intensity, the temperature of the trapped atom sample and the confining power of the trap (spring constant) vary as well. Since collision rates depend on temperature and trap depth, it is important to measure these parameters. This will allow us to compare with theory at a given temperature and also to determine the temperature and trap depth dependences of the various collisional processes.

Temperatures below 1 mK require special measurement techniques. We have used the ballistic time-of-flight method to measure the velocity distribution directly. A sample of trapped atoms is subject to the following sequence of events:

1) The trap laser is quickly (~1 μs) turned off, freezing the atomic velocity distribution and removing the trap potential; 2) The quadrupole magnetic field associated with the trap is quickly (~50 μs) turned off in order to avoid distorting the atomic trajectories; 3) The atoms travel ballistically away from the trap region; 4) A fraction of the escaping atoms pass through a probe laser located below the trap; 5) This causes the atoms to fluoresce, and the time dependence of this fluorescence is a direct measure of the distribution of arrival times of atoms at the location of the probe. This time-of-flight distribution is inverted to give the velocity distribution, and therefore the temperature. We note that at these very low temperatures, gravity dominates the motion of the free atoms , so that a higher temperature results in a broader time-of-flight curve but does not affect the peak arrival time significantly.

We have made extensive measurements of temperature for both isotopes as a function of trap laser intensity for several different tunings of the trap laser. The temperatures are generally well below the Doppler limit (141 μK for Rb) with minimum values in the range of 10 μK. For the most part, temperature varies linearly with intensity and inversely with detuning. These trends are consistent with sub-Doppler cooling mechanisms seen in optical molasses. In fact, we find no discernable difference between temperatures in a MOT and temperatures in optical molasses (i.e., magnetic field turned off) with the same polarization. There is a small difference between the isotopes, with ^{87}Rb having slightly higher temperatures than ^{85}Rb. Our measured temperatures compare remarkably well with three-dimensional, multi-state, semi-classical simulations.

The trapped atoms are confined in an effective potential well due to the spatially varying forces exerted by the laser beams. The size of the trapped atom cloud reflects both the temperature and the restoring force of the potential. A lower temperature T or larger spring constant k (tighter confinement) results in a smaller cloud, with the size varying as $(T/k)^{1/2}$. The size is measured by analyzing a digitized image of the trap taken with a CCD camera. Using our time-of-flight temperature measurements, we can thus determine the values of k.

Our measurements show that the spring constant is independent of intensity at high intensity but decreases at low intensity. It varies inversely with detuning and does not display a significant isotopic dependence. These trends are again consistent with sub-Doppler cooling mechanisms. It is interesting that the sub-Doppler cooling and restoring forces both break down at low intensity, but at rather different values, suggesting different mechanisms for the cooling and restoring forces. The fact that we see no dramatic difference in temperature or spring constant between the isotopes is very significant. Our previous work revealed a large isotopic difference in the rate of escape of atoms from the trap. We

can now definitely say that this difference is collisional in nature and most likely attributable to hyperfine structure.

This previous work gives us some information about the ability of the trap to confine atoms which have undergone an exoergic inelastic collision, such as a hyperfine-state changing collision. The dependence of the collisional trap loss rate on trap intensity and isotope indicate that the velocity dependent forces are more important than the position dependent forces in determining whether escape occurs. We have performed detailed simulations of the trap which support this idea. However, these simulations do not display the same dependence of loss rate on intensity which was observed in the experiments. This is an important issue because one must understand what determines escape if one is going to quantify collisions (such as radiative escape) which do not result in an obvious product (i.e., change of state). Efforts to understand this discrepancy, and the possible role of trap anisotropy, are continuing.

The fact that the two isotopes of Rb have different collisional properties implies that it would be interesting to investigate collisions between the two isotopes. Such mixed isotope collisions obviously require that both isotopes be trapped simultaneously. We have successfully done this using two independent diode lasers to form overlapping traps. Loading of this dual trap is accomplished by multiplexing the laser which slows the atomic beam so that it switches between isotopes on alternate chirps.

In all alkali atoms, hyperfine structure is a complicating factor. The first evidence that it plays an important role in ultracold collisions was our previous work examining the isotopic differences in collisional properties of laser-trapped Rb. We found that under identical conditions the rate of trap loss collisions between a ground- and excited-state atom was a factor of ~3 larger for ^{85}Rb than for ^{87}Rb. Subsequent work by the Walker group revealed that the trap loss spectra, i.e., the trap loss rates as functions of the frequency of a separately applied "catalysis" laser, were also significantly different for the two isotopes. However, these spectra had large gaps near the atomic hyperfine resonances due to the fact that the catalysis laser causes severe optical pumping and significantly perturbs the trap when resonant with these transitions. Unfortunately, this is the most interesting region in terms of collisions. Paul Lett (NIST, Gaithersburg) and Klaus Molmer (Aarhus) developed a model for these collisions which includes the effects of excited-state hyperfine structure. It is basically an extension of the Gallagher-Pritchard model which allows for the three relevant excited-state ($5p_{3/2}$) hyperfine levels of ^{85}Rb (F'=4,3,2). We were able to test this model by examining the collisional loss rate in ^{85}Rb at frequencies very near the atomic hyperfine resonances.

We measured the collisional trap loss rate β as a function of laser frequency by illuminating the trap with a separate tunable laser. The difficulty in these measurements was due to the fact that this laser can have a large effect on the trap itself when it is tuned near one of the atomic hyperfine resonances. Therefore, it was necessary to operate at extremely low intensities (e.g., 50 $\mu W/cm^2$) in order to avoid perturbing the trap. Fortunately, our nonlinear decay method is capable of measuring very small changes in β. Furthermore, we were able to operate the trap in a regime where, due to the low temperature suppression effect (described below), the rate of trap loss collisions induced by the trap laser was extremely low.

The experimental data and the prediction of the model agree fairly well, with both showing large peaks in the vicinities of the atomic hyperfine resonances. Our results are also in reasonable agreement with earlier, but less comprehensive results from the Walker group.

There have been recent predictions that the rate of trap loss collisions involving a ground- and excited-state atom should decrease dramatically as the temperature is lowered. Laser light tuned near resonance causes excitation to a long-range attractive potential at large R. An important issue in determining whether an observable (e.g., ΔJ) collision takes place is that of survival of the excitation from large R to small R. For small negative detunings, the attractive potential is relatively flat where the excitation takes place (large R) and the initial collisional velocity plays a dominant role in determining whether the excited atom can reach short range before spontaneous decay occurs. If this velocity is low, survival of the excitation is unlikely. Therefore, it is predicted that the rate of these collisions should be dramatically reduced at low temperatures. This prediction is based on a localized excitation, as occurs in a Landau-Zener model.

We have experimentally observed this predicted suppression. The temperature is varied by changing the trap laser intensity. Since the collisions process involves a ground- and excited-state atom, the rate should increase in proportion to the intensity, regardless of the temperature dependence. Therefore, we divide the collision rate by intensity to remove this expected dependence. Our knowledge of the temperature as a function of the trap laser intensity then allows us to extract the temperature dependence of the intensity-normalized collision rate β*. We indeed observe an obvious suppression of β* for temperatures below ~70 μK. We carefully considered several issues in interpreting this data: ground-state hyperfine-changing collisions; saturation of the collision rate; the effects of radiative escape; and the possibility that atoms are localized in wavelength-scale potential wells, and concluded that none of them can explain the observed suppression. Therefore, we claim that our observations are consistent with the predicted low-temperature collisional suppression. Such an effect may have

important implications for efforts to achieve colder and denser samples of trapped atoms.

Publications:

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"Suppression of Trap Loss Collisions at Low Temperature," C.D. Wallace, V. Sanchez-Villicana, T.P. Dinneen, and P.L. Gould, Phys. Rev. Lett. **74**, 1087 (1995).

5/1/95-4/30/98 Progress Report:

We completed a comprehensive investigation of the collisional properties of a Rb MOT. Trap-loss collisions of both ^{85}Rb and ^{87}Rb were examined over a wide range of trap laser intensities and detunings. The following trend were observed. At low intensities and/or large detunings, the trap is sufficiently shallow that products of hyperfine-changing (ΔF) collisions between ground-state atoms can escape, resulting in a large loss rate. For a given detuning, as the intensity is increased, the trap becomes deeper. Therefore, the loss rate decreases sharply as this collisional escape channel is closed. However, for larger detunings, the intensity required to close this channel is higher. This indicates, that under our conditions, the confining power of the trap degrades rapidly as the detuning is increased. We have performed numerical simulations of the trap recapture process which confirm this conclusion. These simulations account for the three-dimensional aspects of the light field (three mutually orthogonal pairs of counterpropagating and oppositely-circularly-polarized Gaussian beams), the spatially-varying magnetic field, and the multiple magnetic sublevels of the atom. Results agree quite well with the experimental data for both isotopes. We have also carried out simpler one-dimensional simulations which verify the observed trends.

If the trap intensity is increased beyond that necessary to close the ΔF escape channel, the trap loss rate β begins to rise. This is due to collisions between ground- and excited-state atoms. For small detunings, the low-temperature

suppression effect results in a pronounced minimum in the loss rate. This low value of β ($<10^{-13}$ cm^3s^{-1}) is important in all of our multiple-laser experiments because it allows us to operate under conditions where collisions caused by the trap itself can be neglected.

In addition to measuring trap-loss rates due to inelastic collisions between cold atoms, we have also determined loss rates due to elastic collisions with room-temperature background-gas atoms. As the confining lower of the trap is reduced (by decreasing the intensity or increasing the detuning), we see an increase in this loss rate. Surprisingly, the observed rate of increase is much higher than predictions based on a simple classical model.

Inelastic collisions which lead to trap loss are an impediment to achieving high densities of trapped atoms. Turning off or suppressing such collisions is therefore a worthy goal. We have succeeded in doing this with ground-state hyperfine-changing (ΔF) collisions of ^{87}Rb. By exciting (with blue-detuned light) the colliding atoms to a repulsive molecular potential at long range, we prevent them from approaching closely enough for the inelastic process to occur. The atoms are essentially "shielded" from short-range interactions. This shielding only works for slow atoms because their low kinetic energies allow them to be turned around easily and also because the interaction becomes more adiabatic for lower velocities.

In the experiment, we operate the trap at sufficiently low intensity that ΔF collisions lead to escape. The collisional loss rate is therefore very high. We then apply the suppression laser and measure the reduction in the loss rate. The reduction factor is observed to increase as a function of suppression intensity. At our maximum intensity, we are able to suppress the rate of collisions by about 50%. The measurements are consistent with a simple Landau-Zener model. In this picture, the long-range excitation, and therefore the suppression, becomes more effective at higher intensities as the interaction becomes more adiabatic. We note that, under some conditions, the shielding process is elastic. Since we can adjust (via the laser tuning) the radius at which the repulsion occurs, we can, in principle, enhance the rate of elastic collisions between cold atoms.

Laser excitation of an atom pair to an attractive potential can lead to an observable inelastic collision if the excitation survives to short enough range. However, even if the excitation doesn't survive, there can still be a dramatic effect on the atomic trajectories. The atoms gain kinetic energy and are redirected by the attractive force, resulting in an enhancement of the collisional flux at short range. We have observed this effect in a two-laser experiment. The first laser (the trap laser) is tuned just below the atomic resonance (e.g., detuning $\Delta_t=-1\Gamma$, where $\Gamma=2\pi(5.9\ MHz)$ is the natural linewidth), thereby exciting atom pairs at long range

(e.g., R_t=140 nm). Although survival of the excitation to short range is poor, there is significant acceleration and deflection before spontaneous emission intervenes. The second (probe) laser, tuned much farther below resonance (e.g., Δ_p=-100Γ), intercepts this enhanced flux and re-excites it at intermediate range (e.g., R_p=30 nm). Survival of this second excitation is quite likely, resulting in a short-range inelastic trap loss process. The signature of this cooperative effect is a collisional loss rate with both lasers present which exceeds the sum of the loss rates due to each laser individually.

The experiment is performed by chopping the two lasers (trap and probe) and comparing the collisional loss rate when they are chopped in phase versus out of phase. In the first case, since the lasers are present simultaneously, the flux enhancement will be operative. In the second case, the lasers are alternated in time and therefore they act individually. The factor by which the probe-induced collision rate is enhanced by the trap laser increases with the magnitude of the probe laser detuning, reaching a factor of ~3 at Δ_p=-170Γ=2π(1 GHz), the largest detuning we investigated. Obviously, these effects are not small. In fact, such enhancements must be considered in any experiment which uses a separate probe laser (often called a "catalysis" laser) to induce ultracold collisions. Processes such as photoassociation, where the laser-induced molecule formation takes place at relatively short range, may actually benefit from this flux enhancement. Finally, we note that collisional flux enhancement may induce nontrivial density correlations, which at high densities, may become significant.

One of the interesting features of ultracold collisions is that their time scale is rather long (e.g., 10^{-7} s) compared to typical atomic collisions at room temperature (e.g., 10^{-12} s). Of particular significance is the fact that radiative lifetimes are typically 10^{-8} s, indicating that spontaneous decay of excited states is quite likely to occur during the course of the collision. Since most trap-loss collisions occur at short range and involve excited potentials, this decay is obviously a crucial factor in determining the rate of collisions.

Using the flux enhancement effect discussed above, we have been able to observe collisions of ^{85}Rb in real time. This work was featured in Science [J. Glanz, Research News (Physics): "The Subtle Flirtation of Ultracold Atoms," Science **280**, 200 (1998)].

The experiment employs a pump-probe arrangement with pulses from two separate lasers (trap and probe) to follow the temporal evolution of the collisional trajectories. The trap laser is tuned close to resonance and excites atom pairs at long range (e.g., R>100 nm). Under the influence of the attractive potential, the atoms are accelerated and deflected until spontaneous emission occurs, which turns off the attractive force. The atom pair thus proceeds to short range on the nearly flat ground-state potential. The probe laser, tuned well below resonance, intercepts

this enhanced flux of atom pairs and excites them at intermediate range (e.g., R~25 nm). Following this second excitation, the atoms are further accelerated and undergo an observable inelastic collision at short range (e.g., R~7 nm). We define the collision time as the time to travel from the first excitation radius (R_t) to the second excitation radius (R_p). By pulsing the two excitations, and measuring the collisional loss rate as a function of delay between the pulses, we can map out the distribution of collisions times. This type of measurement can be viewed as a stroboscopic following of these very slow collisions in real time.

Semiclassical numerical simulations of these collisions have been performed and compared to the experimental data. Ignoring hyperfine structure, there are five attractive potentials (Hund's case (c)) which can be excited at long range: 1_u, 2_u, 0_g^-, 0_u^+, and 1_g. Since their long-range potential coefficients (C_3) and radiative lifetimes differ, they will each have a characteristic distribution of collision times. Comparing to the data, we find that the longer-lived states (1_u and 2_u) seem to contribute most strongly. This type of comparison may be useful in sorting out the roles of the various long-range hyperfine curves in trap-loss collisions.

Collisions involving the highly-excited Rb 5D level would form an interesting contrast with those involving the 5P level, which we have studied extensively. The 5D is longer lived and the molecular potentials are shorter range (R^{-6} for 5D vs. R^{-3} for 5P), meaning that survival of the excitation to short range should be more likely. In the context of looking at collisions involving the 5D level, it is of interest to investigate schemes for efficient excitation of this state. Two photons are necessary to reach the 5D state from the 5S ground state: one at 780 nm to drive the 5S$\rightarrow$5P transition and one at 776 nm to drive the 5P$\rightarrow$5D transition. One might think that the most efficient route would be to first populate the 5P intermediate state and then transfer this population to the 5D state. However, the efficiency of each step is very sensitive to details of the laser pulses, and in addition, the intermediate state undergoes radiative decay during the excitation. It has been shown that population transfer in a three-level lambda system can be essentially 100% efficient if the pulses are arranged in the counterintuitive order, i.e., with the second transition driven first. This is due to an adiabatic evolution of the system from the initial state to the desired final state with negligible coupling to the short-lived intermediate state. Because of the importance of adiabaticity, this situation has been designated "Stimulated Raman Adiabatic Passage" or STIRAP.

We have demonstrated that this counterintuitive pulse ordering can also be used to efficiently transfer population in a three-level cascade system, specifically the 5S$\rightarrow$5P$\rightarrow$5D system in Rb. Our experiments use trapped Rb atoms as the sample and the pulses are generated by switching diode laser light with acousto-optic modulators (AOMs). The 5D population is monitored via the 420 nm

fluorescence emitted in the second step of the 5D→6P→5S cascade decay. The excitation efficiency is measured as a function of delay, and the absolute efficiency is determined by comparing its saturation behavior with that predicted by numerical simulations. The measured efficiency does approach 100% and is optimized for counterintuitive pulse ordering. The only aspect of the data which is somewhat puzzling is the fact the absolute laser intensities must be adjusted significantly to give good agreement between the measurements and the simulations.

Publications:

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5/1/98-4/30/01 Progress Report:

In our previous work, we measured ground-state hyperfine (ΔF) collision rates for both ^{85}Rb and ^{87}Rb in a MOT. The two isotopes has similar rate constants in the range of 10^{-11} cm^3s^{-1}. These rates were determined by observing the large jump in the trap-loss rate when the trap laser intensity was lowered below a critical value, resulting in a trap shallow enough to allow the products of a ΔF collision to escape. The apparent plateau in the loss rate at low intensities was interpreted as

the ΔF collision rate. Meanwhile, experiments at JILA showed that a mixed-spin-state ^{87}Rb BEC had an anomalously small low-temperature (~1 μK) spin-exchange rate. Since spin-exchange collisions are closely related to ΔF collisions, the JILA BEC results could be used to predict what we should see at our higher MOT temperatures (~100 μK). Our measured ΔF collision rates were higher than these predictions by well over an order of magnitude. Subsequent BEC experiments further constrained the Rb_2 ground-state potentials and confirmed this discrepancy.

Assuming that the presence of MOT laser light was somehow responsible for the disagreement, we devised a population switching technique for measuring the ^{87}Rb ΔF collision rate in the dark. We turn the trapping and repumping lasers off during a "dark" period. If the atoms are in the upper hyperfine level, which is normally the case in a MOT, they can undergo (only) ΔF collisions during this dark period. However, we can optically "depump" them into the lower hyperfine level at the beginning of the dark period, thereby turning off all collisions. The difference in collision rates between these two situations is simply the ΔF collision rate in the dark. Comparing the rate in the dark to that in the light, we found that indeed there is a large enhancement (up to a factor of 30) caused by the laser light. Concurrent experiments by the Walker group (UWisconsin) found a ΔF collision rate which increased with trap laser intensity, also indicating a light-induced effect. The origin of this enhancement has yet to be established.

In addition to observing the dramatic effects of laser light on the ΔF collisions, we were able to compare our measured dark collision rates with theoretical predictions from our colleagues at NIST (Paul Leo, Eite Tiesinga, and Carl Williams). Furthermore, by varying the trap laser intensity, we were able to measure the temperature dependence of the dark collision rate. The overall rates compare quite favorably, but the measured rate increases significantly faster with temperature than does the predicted rate.

We have measured the wavelength dependence of the Rb($5D_{5/2}$) photoionization cross section using a variation of our previously demonstrated trap-loss technique. A cold sample of ^{85}Rb is efficiently excited to the $5D_{5/2}$ level by the two-photon transition: $5S_{1/2} \rightarrow 5P_{3/2} \rightarrow 5D_{5/2}$, with pulses in the counterintuitive order, i.e., the upper transition is driven first. This is a variation of the STIRAP (stimulated Raman adiabatic passage) technique. The diode laser pulses are repeated at 50 kHz, which accounting for the 241 ns lifetime of the $5D_{5/2}$ level, provides a time-averaged excited-state fraction of <1%. When we apply cw light with $\lambda < 1.25$ μm, we photoionize the $5D_{5/2}$ level at a time-averaged rate which is proportional to the photoionization intensity. Since an ionized atom is no longer trapped, the photoionization rate is reflected in the increased loss rate of atoms from the trap. The trap is loaded at a constant rate from the background vapor, so

an increased loss rate results in a reduced steady-state number of trapped atoms. We have also performed measurements with pulsed photoionizing light. Here we time the pulse (~5 ns wide) to arrive immediately following the $5D_{5/2}$ excitation. The intensity is high enough to produce significant ionization in a single shot, resulting in a measurable depletion of the trap every time the pulsed laser fires. In fact, we can saturate the ionization, so that every $5D_{5/2}$ atom is ionized in one pulse. This is used to calibrate the efficiency of the $5D_{5/2}$ excitation. Under saturated conditions, the fraction of trapped atoms which disappears following a pulse is the fraction of atoms which were in the $5D_{5/2}$ level when the pulse arrived.

Using different laser sources, we have measured the wavelength dependence of the $5D_{5/2}$ photoionization cross section. Hossein Sadeghpour at ITAMP has calculated this cross section, and the agreement is quite satisfying. Our measurements are not only good tests of the atomic structure calculations, but also important for any experiments involving the Rb($5D_{5/2}$) level, e.g., ultracold collision measurements. The excitation light (780 nm and 776 nm) is capable of photoionizing this level, so this loss mechanism must be accounted for.

Most of our measurements to date have utilized a MOT which was loaded from a chirp-cooled atomic beam. This apparatus required significant maintenance and was subject to vibrations from the vacuum pumps. We recently eliminated the atomic beam and switched to a double-MOT apparatus based on the LVIS (low-velocity intense source) design. A "source" MOT captures and cools atoms from a relatively high pressure background vapor. These atoms are pushed into an ultrahigh vacuum (UHV) chamber where a second "UHV" MOT is located. Because of the low background pressure (~10^{-10} torr), this MOT has a long decay time, allowing sensitive measurements of trap-loss collisions. As with our original chirp-cooled atomic beam, we can turn off the loading and monitor the decay of the trapped sample. The reduced vibration, in conjunction with improved diode-laser frequency stabilization and more efficient fluorescence collection, has resulted in an increased signal-to-noise ratio and higher quality decays.

Another improvement in the apparatus is the incorporation of a phase-stable MOT. A standard MOT uses three beams, derived from a single laser, which are retroreflected to provide the six confining beams. The relative time phases of the three pairs of beams where they intersect in the MOT is determined by the different path lengths from where they are split. These phases are important because they determine the polarization pattern of the three-dimensional light field which can have subtle effects on the properties of the MOT. For example, for two orthogonal standing waves with orthogonal linear polarizations, the light will be linearly polarized for equal phases, but circularly polarized for a time phase difference of $\pi/2$. Since we do not actively control these phase differences in the experiment, they can drift due to thermal expansion and/or atmospheric pressure

variations. We believe that phase-induced variations in the trapped cloud volume have limited our ability to extract accurate collisional rates.

To avoid this problem, we have adopted a different configuration of MOT beams. Instead of retroreflecting each arm, the trap laser is split once, into two beams of equal intensity, and each beam travels through each arm, but in opposite directions. In this configuration, the two counterpropagating beams form a single standing wave (which is folded on itself) with a single, well-defined time phase. We have observed more stable decays and less drift in trap parameters (especially volume) with this arrangement.

A MOT requires not only a trapping laser, but also a repumping laser which differs in frequency by typically a few GHz. For Rb, two separate diode lasers are usually used. However, by applying frequency modulation via the injection current, the appropriate sidebands can be generated from a single diode laser. We have combined this modulation with optical injection locking, yielding a high-power, two-frequency, frequency-stabilized diode laser. An external-cavity "master" diode laser is frequency-stabilized near an atomic resonance, and a small fraction of its power is injected into a "slave" diode laser. The slave frequency locks to that of the master. We then modulate the slave current at a few GHz, producing sidebands. For both isotopes of Rb, the relevant sideband for repumping has a least 2% of the power, which is more than enough for MOT operation. Since the diagnostics (e.g., frequency stabilization) are done on the master laser, all of the slave laser's power is available for the experiment. This simplified set-up will be especially convenient in experiments requiring simultaneous trapping of both Rb isotopes.

Publications:

"Ultracold ^{87}Rb Ground-State Hyperfine-Changing Collisions in the Presence and Absence of Laser Light", S.D. Gensemer, P.L. Gould, P.J. Leo, E. Tiesinga, and C.J. Williams, Phys. Rev. A **62**, 030702(R) (2000).

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5/1/01-3/31/04 Progress Report:

Ultracold collisions involving the highly-excited 5D level are an interesting contrast to the extensively studied 5P collisions. The R^{-6} interaction potential for 5S+5D atoms is significantly shorter range than the R^{-3} potential for 5S+5P. Also the radiative lifetime of the 5D level is much longer than that of the 5P: 240 ns vs. 27 ns. The combination of these factors means that, once produced, the 5D excitation should easily "survive" to short range. The experiments are performed by exciting cold atoms in a vapor-cell MOT with continuous two-photon (780 nm and 776 nm) diode laser excitation: $5S_{1/2} \rightarrow 5P_{3/2} \rightarrow 5D_{5/2}$, and measuring the density-dependent loss rate due to collisions. In addition, the competing density-independent loss rate due to 5D photoionization (caused by both excitation lasers) must be accounted for. We have directly measured this cross section in previous work. Using the trap laser detuning to vary the atomic density, loss rates in a vapor-cell MOT are measured at two different densities. The density-dependent (collisional) and density-independent (photoionization) components of the loss rate are thus determined. This is repeated for different detunings of the 5D excitation. We find that the collisional loss in maximized on resonance. This is consistent with the picture that excitation at long range can survive to short range where an inelastic process (e.g., fine-structure change) can occur, leading to trap loss. The internuclear separation of an excited atom pair is largest, and therefore the number of available pairs is maximized, for resonant excitation. Modeling of these results using the long-range molecular potentials will be required for a complete understanding.

Our frequency-chirped collision experiments, discussed below, require relatively intense (e.g., 100 W/cm^2) light whose frequency is rapidly chirped. We have used a two-laser scheme to produce this light in a controllable manner. The first laser is a narrow-band, yet tunable, external-cavity diode laser (ECDL) with an available output power of ~20 mW. When the drive current of this laser is rapidly modulated, the frequency follows. For example, with a 5 MHz triangle wave current modulation, we can produce a frequency modulation amplitude of 1 GHz, which yields a linear chirp rate of 10 GHz/μs. Unfortunately, this light suffers from significant amplitude modulation. For the above parameters, the output intensity varies by ~30% during the ramp. This is not surprising since a significant current modulation must be used to produce this degree of high-frequency modulation in an ECDL. We circumvent this problem by using a small portion (e.g., 500 μW) of this light to injection lock a second free-running diode laser. This "slave" laser locks its frequency to the "master" laser and follows its chirp. The output power of the slave is independent of the power used to inject it, and therefore remains constant throughout the chirp. As an additional benefit, the

full power of this slave laser (e.g., 50 mW) is available for the experiment. The time variation of the frequency of this system is measured by looking at the heterodyne signal between its light and that from a fixed-frequency reference laser. We have verified that the slave laser does indeed remain locked to the master throughout the chirp by heterodyning their outputs. In addition to being useful for controlling ultracold collisions, this type of chirped light can be applied to atomic excitation via adiabatic passage and studies of coherent transients.

In collaboration with theorists here at UConn and in Armenia and Finland, we have developed a model for photoassociation of a Bose-Einstein condensate (BEC). Starting with a purely atomic BEC, light is adiabatically swept through a photoassociative resonance, thereby converting atoms into bound molecules. The situation is reminiscent of the well-known Landau-Zener model, where two coupled curves cross and the probability of making a transition from one curve to the other depends exponentially on the rate at which the crossing is traversed. In the case of BEC photoassociation, however, the system is nonlinear due to the fact that it takes two atoms to make a molecule. Surprisingly, we find that in this nonlinear case, the no-transition probability is linearly proportional to the rate at which the crossing is traversed. This analytical result, which has been tested numerically, will also apply to controlling the scattering length of a BEC via a Feshbach resonance, second-harmonic generation in nonlinear optics, and any field theory involving these nonlinear terms.

We have obtained very interesting and promising data on trap-loss collisions induced by frequency-chirped light. We illuminate our trapped sample with pulses of chirped light and measure the resulting collisional loss rate. The chirped light is produced using the master-slave arrangement described above, and an acousto-optical modulator (AOM) is used to select a short pulse (e.g., 40 ns) within each chirp. A sequence of these pulses is applied during a period when the MOT lasers are off. We have verified that the collisional loss rate increases linearly with the number of pulses, as it should. Varying the intensity of the chirped light, we find that the collisional loss rate saturates at high intensities, as expected when the chirped excitation becomes adiabatic. We have also measured the loss rate as a function of delay between successive pulses. At short delays, the rate is suppressed, indicating that the atom pairs available to be excited by a given chirp have already been caused to collide inelastically by the preceding chirp. A finite time is required for these depleted atom pairs to be replenished by the thermal motion. At long delays, each chirp is acting independently. In between, there is a peak in the loss rate, indicating that successive chirps are acting cooperatively. The long-range collisional flux initiated by one chirp enhances the number of atoms pairs available for the next pulse. This is reminiscent of our previous work using pulses of fixed-frequency light to map out collision times. Perhaps the most

exciting result is the dependence of the loss rate on the chirp rate. Comparing a fast chirp rate of 25 GHz/μs with a very slow chirp covering the same range of frequencies, we find that the fast chirp yields a much larger rate of trap loss collisions, indicating that each fast chirp excites a large number of atom pairs, causing them to collide inelastically. These results will be compared to numerical simulations for a more complete understanding.

We plan to undertake mixed-isotope collision experiments which will require overlapping MOTs of ^{85}Rb and ^{87}Rb. Although we have demonstrated simultaneous trapping of the two isotopes in the past, our recent experiments have utilized one isotope at a time. Since the resonant frequencies for trapping and repumping differ significantly for the two isotopes, trapping both isotopes requires a duplication of the laser systems. These systems, incorporating frequency-stabilized master lasers and injection-locked slave lasers, have been constructed. In addition, a scheme for separately measuring the fluorescence from the two isotopes is necessary in order to independently monitor their densities. This will be done by alternating (at 10 kHz) the two MOT lasers and time-resolving the fluorescence. This gated detection has been realized by feeding the signal from a single avalanche photodiode (APD) into an rf switch which is synchronized with the alternation of the MOT lasers. When a given MOT laser is switched on, the output of the APD is directed to the appropriate signal channel by the rf switch.

Publications:

"Frequency-Chirped Light from an Injection-Locked Diode Laser", M.J. Wright, P.L. Gould, and S.D. Gensemer, Rev. Sci. Instrum. **75**, 4718 (2004).

"Landau-Zener Problem for Trilinear Systems", A. Ishkhanyan, M. Mackie, A. Carmichael, P.L. Gould, and J. Javanainen, Phys. Rev. A **69**, 043612 (2004).

5/1/04-3/31/07 Progress Report:

We completed and published our first set of experiments on trap-loss collisions induced by frequency-chirped light. Our initial measurements focused on the dependence of the collisional loss rate on both the intensity of the chirped light and the chirp rate. The intensity dependence exhibits the expected saturation as the chirped excitation becomes adiabatic. We employed both positive and negative chirp directions, with 40 ns pulses and with the center frequency of the chirp fixed at 300 MHz below the $5S_{1/2}$ (F=3) -> $5P_{3/2}$ (F'=4) transition (center detuning Δ_c = -300 MHz). We compared the data with the results of theoretical calculations

combining quantum mechanical wavepacket excitation probabilities (calculated by our collaborators Jiri Vala and Ronnie Kosloff) with Monte-Carlo simulations of the trajectories. For these initial parameters, there is not a significant difference between the two chirp directions. However, this is not true in general. As discussed below, we do see significant differences under some conditions, which we interpret as evidence for coherent effects. The dependence of the collisional loss rate on chirp rate shows an enhancement of at least an order of magnitude at our standard rate of 10 GHz/μs compared to the quasistatic situation. This demonstrates that the dynamics of the chirp is important. Just having a range of frequencies present is not equivalent. This work was featured in Nature Physics Research Highlights [E. Gerstner, Light Chemistry, Nature Physics Published online: 11 August 2005, doi: 10.1038/nphys107].

We have extended our work with frequency-chirped light to include multiple pulses. Using two identical chirped pulses separated by a variable delay, we are able to investigate the ultracold collisional dynamics. With this pump-probe configuration, we observe two main effects. First, for a relatively small center detuning of the chirp ($\Delta_c/(2\pi)$ = -300 MHz), the rate of collisions induced by a given pulse (pulse 2) can be increased by the presence of an earlier, appropriately timed, pulse (pulse 1). We attribute this to the enhancement of short-range collisional flux, available for excitation by pulse 2, due to the long-range excitation of atom pairs to an attractive molecular potential by pulse 1. We have previously investigated this flux enhancement using both cw excitation and short-pulse (100 ns) excitation with fixed-frequency light. The second effect we observe is just the opposite: depletion. This occurs for a larger center detuning of the chirp ($\Delta_c/(2\pi)$ = -600 MHz) and short delays (200 ns). In this case, pulse 1 efficiently excites available short-range atom pairs, causing them to undergo trap-loss collisions. If pulse 2 arrives before the thermal motion has had a chance to replenish the depleted pair distribution, there are fewer short-range pairs to be excited and the collision rate is reduced. Such depletion effects are important to consider in any experiment using high-repetition-rate short-pulse lasers for ultracold molecule formation.

In order to simulate our experiments, we have performed Monte-Carlo simulations of the frequency-chirped collisions, treating the motion of the atoms classically. In these simulations, we choose the initial conditions (position and velocity) randomly, consistent with a uniform density and a Maxwell-Boltzmann distribution of velocities. The probability of chirp-induced excitation to the attractive molecular potential is according to the Landau-Zener formula. An excited atom pair accelerates on the attractive potential until a random spontaneous emission occurs, returning the pair to the ground state, which is assumed flat. At a prescribed delay following the first chirp, the second chirp occurs, and the

calculation is continued. If at any point in the calculation, the atom pair arrives at short range (<100 a_0) in the excited state, that particular trajectory is considered a trap-loss event. For each excited molecular potential, a large number of trajectories are run and the fraction leading to trap loss is determined. The results of these calculations agree quite well with our measurements of the delay dependence. We use a modified version of these simulations to compare with our measurements of the trap loss vs. center detuning, described below.

We have investigated the dependence of trap-loss collisions on the center detuning Δ_c of the frequency chirp. The two chirp directions yield dramatically different results. One important difference is that the data for the positive chirp is quite smooth, while that for the negative chirp exhibits significant structure. The key distinction between positive and negative chirps is the motion of the atom pair (or molecular wavepacket) relative to that of the Condon radius, $R_c = (-C_3/h\Delta)^{1/3}$, the radius at which excitation to the attractive $(-C_3/R^3)$ potential is resonant for a laser detuning Δ ($\Delta<0$). The atom pair always moves inward on the attractive excited-state potential, while R_c moves either inward or outward, depending on the sign of the chirp. For a positive chirp, the detuning increases (i.e., becomes less negative) with time, as does R_c. Therefore, after the initial adiabatic excitation, the atom pair and the Condon radius move in opposite directions, with no further interactions. For the negative chirp, the situation is quite different. Here the atom pair and the Condon radius both move inward, and multiple interactions with the laser light can occur. In comparing positive and negative chirps, there are two regimes of particular interest. In the range $\Delta_c/2\pi$ = -500 MHz to 0 MHz, the trap-loss collision rate for the negative chirp is significantly higher than that for the positive chirp. We interpret this as flux enhancement, similar to what we have seen with two pulses, but now occurring within a single chirp. The early portion of the chirp excites an atom pair to the attractive potential at long range. The atoms then accelerate towards each other before spontaneous emission returns the pair to the ground state. The pair becomes resonant with the chirp again, but this time at short range, where trap loss will occur with high probability. Turning now to the range $\Delta_c/2\pi$ = -1000 MHz to -500 MHz, we find that trap-loss collisions for the negative chirp are suppressed relative to the positive-chirp case. We interpret this suppression as "coherent collision blocking". The early portion of the chirp excites an atom pair at intermediate R. Since the atoms and the Condon radius are both moving inward, the pair can become resonant with the chirp again, but with the pair still in the excited state (i.e., before spontaneous emission can occur). In this case, the pair is stimulated back to the ground state, effectively turning off the collision. This is a completely coherent process. Our identification of the incoherent flux enhancement and the coherent collision blocking mechanisms is

based on examining specific trajectories in the Monte-Carlo simulations described above. Results from these simulations are found to describe the data rather well. Our collaborators, Shimshon Kallush and Ronnie Kosloff have performed fully quantum calculations which also show coherent suppression of collisions for the negative chirp. In the quantum picture, this suppression is due to interference caused by multiple interactions between the collisional wavepacket and the light.

Although the master-slave diode-laser system has worked well in providing linear chirps suitable for our frequency-chirped collision experiments to date, it does have limited speed and lacks the ability to produce arbitrary chirp shapes. Looking ahead to future experiments, we have developed a novel system which is capable of much higher speeds and more flexible frequency waveforms. Instead of directly modulating the laser, we take advantage of recent developments in telecommunications technology, and perform external modulation with a fiber-based electro-optical phase modulator (specified at 40 Gb/s). In order to increase the extent of the modulation, we use multiple passes through the fiber loop containing the modulator, and re-injection-lock the diode laser between passes. When the desired modulation has been achieved, the pulse is switched out of the loop with an acousto-optical modulator (AOM) and sent to the experiment. Driving the phase modulator with an arbitrary waveform generator allows us to create arbitrary frequency chirps. For example, we have produced a sinusoidal frequency modulation superimposed on a linear chirp. The frequency as a function of time is measured with a heterodyne technique. We have not explored the ultimate performance speed of this system – we are currently limited by our heterodyne diagnostics. At some point, the injection locking will not be able to follow the modulated frequency, but we see no evidence of this at the linear chirp rates of ~40 GHz/μs (and corresponding chirp range of ~2 GHz) which we have so far achieved.

Publications:

"Control of Ultracold Collisions with Frequency-Chirped Light", M.J. Wright, S.D. Gensemer, J. Vala, R. Kosloff, and P.L. Gould, Phys. Rev. Lett. **95**, 063001 (2005).

"Probing Ultracold Collisional Dynamics with Frequency-Chirped Pulses", M.J. Wright, J.A. Pechkis, J.L. Carini, and P.L. Gould, Phys. Rev. A **74**, 063402 (2006).

"Coherent Control of Ultracold Collisions with Chirped Light: Direction Matters", M.J. Wright, J.A. Pechkis, J.L. Carini, S. Kallush, R. Kosloff, and P.L. Gould, Phys. Rev. A **75**, 051401(R), (2007).

"Generation of Arbitrary Frequency Chirps with a Fiber-Based Phase Modulator and Self-Injection-Locked Diode Laser", C.E. Rogers III, M.J. Wright, J.L. Carini, J.A. Pechkis, and P.L. Gould, J. Opt. Soc. Am. B **24**, 1249 (2007).

4/1/07-3/31/10 Progress Report:

Our earlier work on ultracold collisions induced with frequency-chirped light was done with linear chirps. Following up on our demonstration of the importance of coherent processes, we have investigated the effects of nonlinear frequency chirps to see whether they would enable a further degree of control. The basic idea is to tailor the shape of the chirp in order to better match the temporal dependence of the Condon radius with the variation of R as the atom pair accelerates on the attractive $-C_3/R^3$ potential. Focusing on the region where we see suppression of the collision rate for the negative chirp, we do see a dependence of the collision rate on the detailed shape of the chirp. We compare results for three different chirp shapes: concave-up (positive curvature), linear, and concave-down (negative curvature). We find small but significant differences in the collision rates between the concave-down chirp and the two other cases. These preliminary data demonstrate that we can indeed control the ultracold collisions via the details of the frequency chirp. These differences do not manifest themselves for the case of a positive chirp. In this case, the Condon radius moves outward with time, while the atom-pair separation R decreases with time due to acceleration on the attractive potential. Hence the atom pair comes into resonance at most once, and the detailed shape of the chirp is not important. We compare these nonlinear negative chirp results with quantum mechanical simulations and find that the trends are consistent. We hope that further simulations will help us gain a better understanding of the control mechanism.

We have benefited greatly from a collaboration with Shimshon Kallush and Ronnie Kosloff from Hebrew University on quantum simulations of our ultracold collisional processes. We had previously developed Monte-Carlo simulations, where the atom-pair trajectories were treated classically, to describe the collisions induced by chirped light. Although these matched some of our experimental results rather well, they obviously cannot include the interesting aspects of coherent control. Ronnie Kosloff's group had previously developed the tools to deal with coherent control of photoassociation on ultrafast timescales and were able to adapt these techniques to our much longer (nanosecond) timescales. Briefly, these simulations use the Chebychev polynomial expansion and the mapped Fourier grid method to follow the time evolution of the ground and excited electronic radial

wavefunctions for a pair of atoms. The potential energy curves and the coupling to the time-dependent (chirped) field are included. Initial states are assumed to be zero-energy s-wave scattering states (singlet and triplet states are treated separately) and trap loss is modeled as a short-range absorbing boundary in the excited state.

Although we continue to collaborate with Ronnie Kosloff's group, we now have the capability to run and modify these simulations ourselves. This is important because the long running times and many convergence tests require constant oversight. The computational cost is high because of the wide range of timescales. The initial free-atom motion is very slow, while the propagation on the attractive potential is very fast. As an example, a typical 200 ns trap-loss simulation is done with 0.45 ps time steps, requiring >11 hours on a custom-built dual-quad core machine. These simulations will be easily adaptable to treating bound molecular states and wavepackets. The faster timescales we will pursue in the experiments will actually require less running time.

Controlling the time evolution of the phase (or frequency), as discussed above, is one key aspect of coherent control. The other is controlling the amplitude. We take advantage of the same telecommunications technology and use a fiber-based electro-optic intensity modulator for this purpose. The device itself is very fast (5 GHz bandwidth), so we are once again limited in speed by our electronics. We have used our 240 MHz AWG to produce pulses as short as 2.5 ns FWHM. This is more than a factor of 10 faster than the pulses used previously, but we plan to go even faster. Importantly, we are now well below the typical time scale for spontaneous emission.

This type of intensity modulator is an interferometric (Mach-Zehnder) device. The input light is split into two paths (waveguides) and then recombined to form the output. The relative phase in the two arms, controlled electronically, determines the output intensity. However, in most devices, as the intensity is modulated, the output phase also varies, leading to residual frequency chirp. This becomes particularly significant for short pulses. We have thoroughly characterized this residual chirp and shown that it can be largely compensated using a separate phase modulator.

The phase and amplitude modulation take their toll on the available output power. In order to make up for these losses, we have constructed a tapered amplifier system for amplifying the frequency- and intensity-controlled pulses. This system can provide a gain of at least 20 at 795 nm, and a maximum power of 500 mW. We have seen a gain of 10 for a short pulse at 787, which is well away from the peak of the gain profile. We have recently obtained another tapered amplifier system which, with the appropriate input, will be able to provide a maximum power of 2W at 780 nm.

Our ultracold molecule detection system is operational. We use a nanosecond pulsed dye laser, pumped by the second harmonic (532 nm) of a YAG laser, to detect ground-state Rb_2 molecules by resonantly-enhanced multiphoton ionization (REMPI). The laser excites to an intermediate electronically-excited state and then photoionizes with a second photon. The resulting ions are accelerated by a constant electric field to a Channeltron detector. Time-of-flight (TOF) is used to distinguish Rb_2^+ ions from Rb^+ ions produced by three-photon ionization of atoms through Rydberg states. So far, we have detected ultracold molecules produced by the MOT itself, but the same scheme will work for ultracold molecules produced by chirped light and/or cw photoassociation. The rather narrow 0.2 cm^{-1} bandwidth of the pulsed dye laser will allow vibrationally state-selective detection. In a separate collaborative project (with Bill Stwalley and Ed Eyler) at UConn, we have developed considerable expertise in REMPI detection of ultracold Rb_2. Our knowledge of the relevant spectroscopy will prove invaluable to the work proposed here.

Publications:

"Cold Molecules Beat the Shakes", P.L. Gould, Science **322**, 203 (2008) (invited "Perspective" article).

"Characterization and Compensation of the Residual Chirp in a Mach-Zehnder-Type Electro-Optical Intensity Modulator", C.E. Rogers III, J.L. Carini, J.A. Pechkis, and P.L. Gould, Opt. Express **18**, 1166 (2010).

4/1/10-3/31/13 Progress Report:

Earlier work on trap-loss collisions induced by frequency-chirped light focused on their enhancement by the chirp, multiple-pulse effects, and the difference between positive and negative frequency chirps. In this latter work, we observed that for certain detunings of the chirped light with respect to the $5S_{1/2} \rightarrow 5P_{3/2}$ resonance, the rate of trap-loss collisions for negative chirps is suppressed relative to that for positive chirps. This was attributed to the inherent asymmetry in the collisional process: inelastic trap-loss collisions always involve an atom pair accelerating *inward* on an attractive excited-state molecular potential, while the excitation radius (or Condon radius R_c) moves either *inward* or *outward*, depending on the sign of the chirp. For a negative chirp, the detuning decreases (i.e., becomes more negative) with time, causing R_c to move *inward*, in the same direction as the atomic separation R. In this case, we can have "coherent collision

blocking" where the atom pair is excited at intermediate R early in the chirp and then stimulated back to the ground state at short R later in the chirp, effectively turning off the collision.

The above-described work was done with linear chirps. Following up on our demonstration of the importance of coherent processes, we investigated the effects of nonlinear frequency chirps to see whether they would enable a further degree of control. The basic idea is to tailor the shape of the chirp in order to better match the temporal dependence of the Condon radius with the trajectory of the atom pair as it accelerates on the attractive $-C_3/R^3$ potential. Focusing on the region where we saw suppression of the collision rate for the negative chirp, we do see a dependence of the collision rate on the detailed shape of the chirp. We compare results for the three different chirp shapes: concave-up, linear, and concave-down. For the negative chirp, we find small but significant differences in the collision rates between the concave-down chirp and the two other cases. This demonstrates that we can indeed control the ultracold collisions via the details of the frequency chirp. These differences do not manifest themselves for the case of a positive chirp. In this case, the Condon radius moves outward with time, while the atom-pair separation R decreases with time due to acceleration on the attractive potential. Hence the atom pair comes into resonance at most once, and the detailed shape of the chirp is not important. Comparing these nonlinear chirp results with quantum mechanical simulations, described below, we find that the trends are consistent.

We are collaborating with Shimshon Kallush from ORT Braude and Ronnie Kosloff from Hebrew University (both in Israel) on quantum simulations of our ultracold collisions and ultracold molecule formation. Although we had previously developed Monte-Carlo simulations, where the atom-pair trajectories were treated classically, we felt it was important to step up to quantum calculations if we were to understand the interesting aspects of coherent control. Profs. Kallush and Kosloff had developed the tools to deal with coherent control of photoassociation on ultrafast timescales and were able to adapt these techniques to our much longer (nanosecond) timescales.

Briefly, the simulations for ultracold collisions use a Chebychev polynomial expansion and the mapped Fourier grid method to follow the time evolution of the ground and excited electronic radial wavefunctions for a pair of atoms. The potential energy curves and the coupling to the time-dependent (chirped) field are included. Initial states are assumed to be zero-energy s-wave scattering states (singlet and triplet states are treated separately) and trap loss is modeled as a short-range absorbing boundary in the excited state. On our time scales, spontaneous emission cannot be ignored – it is included as a sink channel. Results from these simulations are compared with experimental measurements for the case of nonlinear frequency chirps, described above, and reasonable agreement is found.

The simulations for molecule formation which we are developing are similar, but we explicitly keep track of the populations of the various vibrational levels of the excited-state and ground-state potentials, as well as the transitions between them. We also include higher partial waves. Since our chirps span a limited bandwidth (typically 1 GHz in 100 ns), we restrict the simulation bandwidths to a narrow range surrounding those states which can be populated. This keeps the running time manageable. Spontaneous emission is once again included. Simulation results are compared to the data from the molecule formation experiment discussed below, and the agreement is found to be quite good.

We previously developed a new system for producing fast and arbitrary frequency chirps. The scheme is based on a phase modulator, specifically the type of fiber-based device developed for the telecommunications industry. Since frequency is the time derivative of phase, a desired chirp (frequency vs. time) can be realized by building up the appropriate phase vs. time. For example, a linear chirp requires a phase that increases quadratically in time. With the phase modulator, the phase is proportional to the applied voltage. Driving the modulator with an arbitrary waveform generator (AWG) thereby allows the generation of arbitrary (within the speed limit of the AWG) and controllable chirps. We can increase the extent of the modulation by using multiple (e.g., 10) passes through the fiber loop containing the modulator, synchronizing the phase modulation in each pass and re-injection-locking the diode laser source between passes. When the desired modulation has been achieved, the pulse is switched out of the loop with an acousto-optical modulator (AOM) and sent to the experiment and/or heterodyne diagnostics. With this scheme, for example, we can produce a fast linear chirp, ~0.2 GHz/ns, a chirp rate which is a factor of 20 higher than what was used in our recent ultracold collision and molecule formation experiments. With the appropriate electronics, we can push this technology to even higher speeds. Since the chirp rate is the second derivative of the phase, faster chirps can be realized with only a single pass through the phase modulator. With our newly acquired 4 GHz (8 GSample/s) AWG, we expect to gain another order of magnitude in speed. Our modulator is capable of a total phase change of $\sim 10\pi$, which will allow us to chirp >5 GHz in 2 ns with a single pass.

Our phase modulator has also been used to produce arbitrary line spectra. Frequency is the time derivative of phase, so a linearly varying phase yields a fixed frequency offset. Applying a sequence of voltage ramps to the phase modulator, we generate a series of sidebands whose offsets from the carrier are determined by the slopes of the corresponding ramps. We have demonstrated offsets in the 100 MHz range, which was limited by our electronics. Our new AWG will enable significantly larger offsets. This type of multifrequency light may prove useful in the efficient excitation (e.g., for cooling) of multilevel atoms or molecules.

Controlling the time evolution of the phase (or frequency), as discussed above, is one key aspect of coherent control. The other is controlling the amplitude. We take advantage of the same telecommunications technology and use a fiber-based electro-optic intensity modulator, with 5 GHz bandwidth, for this purpose. Using our 4 GHz AWG, we have recently realized pulse widths down to 0.5 ns. This is almost two orders of magnitude faster than the pulses used in our recent experiments Importantly, we are now well below the typical time scale (e.g., 20 ns) for spontaneous emission.

It turns out that the MOT itself can produce ultracold molecules at a reasonably high rate, presumably via photoassociation by the MOT light which is tuned slightly (e.g., 10 MHz) below the atomic resonance. We have used these molecules to optimize our detection of molecules in high-vibrational (v'') levels of the ground state (either X $^1\Sigma_g^+$ or a $^3\Sigma_u^+$). This detection utilizes resonantly-enhanced multiphoton ionization (REMPI) with a nanosecond pulsed dye laser. Excitation to an intermediate electronically-excited state is followed by photoionization by a second photon. The resulting ions are accelerated to a Channeltron detector, and time-of-flight (TOF) is used to distinguish Rb_2^+ ions from Rb^+ ions produced by three-photon ionization of atoms through Rydberg states. Scanning the REMPI laser yields a broad peak at ~601.9 nm from high-v'' molecules. Interestingly, there is a dramatic difference between ^{85}Rb and ^{87}Rb, with the former yielding a much higher rate of MOT-produced molecules. This may be due to the large negative scattering length of ^{85}Rb, indicating that the highest v'' level is barely bound and at very long range. The MOT-formed molecules constitute a significant background in our photoassociation experiments. Furthermore, the MOT-produced $^{85}Rb_2$ is readily destroyed by a separate photoassociation laser. For these reasons, we switched to ^{87}Rb for our molecule formation experiments.

Using this REMPI detection, we have made the first steps in studying the formation of ultracold molecules by frequency-chirped photoassociation. We have chosen a PA line detuned ~7.8 GHz below the $5S_{1/2}$+$5P_{3/2}$ asymptote and used a chirp of 1 GHz in 100 ns, selecting the central portion with a 40 ns FWHM intensity pulse. By measuring the Rb_2^+ signal as a function of the number of PA chirps, and accounting for loss from photodestruction and ballistic escape, we are able to extract the molecular formation rate. We then measure this rate as a function of intensity for the different chirp directions and for unchirped pulses. The key finding is the dependence on chirp direction: the positive chirp produces significantly more molecules than the negative chirp. Somewhat surprisingly, unchirped pulses produce more molecules than either chirp direction. However, if we account for the narrow bandwidth of the unchirped pulses and compare at the same intensity per unit bandwidth, then both chirp directions outperform the

unchirped case. In order to understand the chirp dependence, we have carried out quantum simulations, described earlier, and compared them to the data. They describe the experimental trends rather well. Examining the temporal evolution of the various state populations, we have identified the following mechanism. Following PA to an excited bound level, the positive chirp can drive a transition *down* to a ground-state bound level: a $^3\Sigma_u^+$ (v''=39). This cannot occur for the negative chirp because this bound-bound transition is resonant *before* the free-bound PA transition. On our time scale, a significant fraction of the overall ground-state population results from spontaneous decay of the PA level, which is independent of chirp direction. However, the difference between the two chirp directions is due to the coherent stimulated emission process. Going to faster chirps, as discussed above, should enhance this coherent aspect.

Publications:

"Coherent Control of Ultracold ^{85}Rb Trap-Loss Collisions with Nonlinearly Frequency-Chirped Light", J.A. Pechkis, J.L. Carini, C.E. Rogers III, P.L. Gould, S. Kallush, and R. Kosloff, Phys. Rev. A **83**, 063403 (2011).

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"Production of Ultracold Molecules with Chirped Nanosecond Pulses: Evidence for Coherent Effects", J.L. Carini, J.A. Pechkis, C.E. Rogers III, P.L. Gould, S. Kallush, and R. Kosloff, Phys. Rev. A **87**, 011401(R) (2013).

4/1/13-3/31/17 (including one-year no-cost extension) Progress Report:

Our initial work on molecule formation by chirped photoassociation (PA) focused on the difference between positive and negative frequency chirps. For these measurements, we used a relatively slow chirp, 1 GHz in 100 ns, selecting the central portion with a 40 ns FWHM intensity pulse. The chirp was centered on a PA line detuned ~7.8 GHz below the $5S_{1/2}$+$5P_{3/2}$ asymptote. Using REMPI detection of the resulting molecules, we measured the Rb_2^+ signal as a function of

the number of PA chirps, and accounting for loss from photodestruction and ballistic escape, were able to extract the molecular formation rate. We found that the positive chirp significantly outperforms the negative chirp. By running quantum simulations of the PA process, we identified the mechanism responsible for the enhanced formation rate of the positive chirp. Following PA from the free-atom continuum *up* to the 0_g^- (v''=78) excited bound level, the positive chirp can drive a transition *down* to a ground-state bound level: a $^3\Sigma_u^+$ (v''=39). This works because the downward transition to the bound state is at a higher frequency that the upward (PA) transition from the continuum. On the time scale of these chirps, spontaneous decay of the excited state, which is independent of chirp direction, is not negligible, and indeed is responsible for a significant fraction of the overall ground-state population. The *difference* in formation rates between the two chirp directions can be attributed to the coherent stimulated emission process. Going to faster chirps and higher intensities is predicted to enhance this coherent aspect, while diminishing the role of spontaneous decay. For the chirp rates used here, unchirped pulses produce more molecules than either chirp direction. This again is due to the large contributions from spontaneous emission. Results of our quantum simulations describe the experimental trends rather well.

In order to understand the dependence of molecular formation rate on chirp parameters, we continue to collaborate with Shimshon Kallush from ORT Braude and Ronnie Kosloff from Hebrew University (both in Israel) on quantum simulations of our chirped photoassociation. This has been a very fruitful joint effort as Profs. Kallush and Kosloff have developed the tools to deal with coherent control of photoassociation on ultrafast timescales and were able to adapt these techniques to our much longer (nanosecond) timescales. We have a joint grant from the U.S. – Israel Binational Science Foundation (BSF) which facilitates this collaboration via support of travel by my group to Israel and vice versa.

We have recently published a rather complete description of these simulations of the ultracold molecular formation. We employ a Chebychev polynomial expansion and the mapped Fourier grid method to follow the time evolution of various vibrational levels of the excited-state and ground-state potentials. The dynamics is driven by the coupling between the potentials due to the time-dependent (chirped) field. Since our chirps span a limited frequency range (typically 1-2 GHz), we restrict the basis sets to narrow bandwidths surrounding those states which can be populated. This keeps the running time manageable. On our time scales, spontaneous emission is important. We model it as a set of sink channels to the various vibrational levels of the ground state, as well as its continuum. The contributions of higher partial waves, typically up to J=5, are included. In the simulations, we have also explored other ways, besides the shape of the chirp, to improve the molecular formation rate. Using higher intensities will

certainly help, since the formation rate for this two-photon process is quadratic in intensity. Also, using a different vibrational level in the excited state, $0_g^-(v'=31)$ instead of $0_g^-(v'=78)$, which has better Franck-Condon overlap with the ground state, is predicted to give at least two orders of magnitude improvement. Finally, using two frequencies, which are synchronously chirped, will allow us to access more deeply bound levels in the ground state.

Although we continue to collaborate with Profs. Kallush and Kosloff, we now have the capability to run and modify these simulations ourselves. This is important because the long running times and many convergence tests require constant oversight. The computational cost is high because of the wide range of timescales. The initial free-atom motion is very slow, while the propagation on the attractive excited-state potential can be very fast. As an example, a typical 200 ns molecule formation simulation is done with 0.075 ps time steps, requiring ~3 days on a custom-built 44-core machine. As we go to faster timescales, the experiments become more challenging, but the simulations will actually require less running time.

In coherent control, interfering pathways are employed to enhance a global objective. This is often achieved theoretically via an iterative process which is implemented by solving optimal control theory equations. In our case of molecule formation, the long run times make this impractical. A simpler alternative is local control, a unidirectional and noniterative time propagation scheme which adjusts the field at each instant of time in order to optimize the target at the next time step. We used local control of the phase to optimize the photoassociative production of ultracold $^{87}Rb_2$ molecules in a specific bound level of the lowest triplet state. These simulations yielded an interesting optimum frequency evolution (chirp) for a Gaussian intensity pulse. In the first half of the pulse, the light should be resonant with the photoassociation transition to the excited state. Then it should jump rapidly to the stimulated emission transition, driving the excited-state population down to the target state. We explored variations of this scheme, including the simultaneous presence of two frequencies and the effects of sudden jumps in phase as well as frequency. The predicted efficiency of this rapid frequency jump, compared to that for a linear chirp, inspired us to incorporate a similar chirp in the experiment, as described below.

In an effort to increase our yield of ultracold molecules, we took advantage of our technical improvements in producing chirped pulses, as well as the insight gained from our local control simulations, described above. By employing shaped frequency chirps on 2.7x faster time scales and at 2x higher intensities, we were able to achieve significant enhancements. More specifically, we found that a positive piecewise linear (PPL) chirp, where the chirp was slow-fast-slow, significantly outperformed the positive linear (PL) chirp, as well as the negative

linear (NL) chirp and unchirped pulses. This PPL shape was inspired by the rapid frequency jump which emerged from the local control optimization. It has the following advantages relative to the PL chirp: 1) the frequency passes through the photoassociation and stimulated emission resonances relatively slowly, and therefore more adiabatically; 2) the frequency jumps between the two resonances quickly, thus lessening the effects of spontaneous emission; and 3) this rapid jump results in both resonances being reached near the peak of the pulse and therefore at higher intensity. We note that these improvements resulted in an optimum formation rate at least an order of magnitude higher than in our earlier work, despite a 2.3x lower chirped pulse repetition rate. The measured formation rates for the various chirps agreed quite well with the quantum simulations.

We have refined our system for producing fast and arbitrary frequency chirps and intensity pulses. The chirps are generated with a phase modulator, specifically the type of fiber-based device developed for the telecommunications industry. Since frequency is the time derivative of phase, a desired chirp (frequency vs. time) can be realized by building up the appropriate phase vs. time. For example, a linear chirp requires a phase that increases quadratically in time. Driving the modulator with an arbitrary waveform generator (AWG) allows the generation of arbitrary (within the speed limit of the AWG) and controllable chirps. For the molecule formation experiments described above, we used multiple (e.g., 4) passes around a fiber loop containing the modulator in order to build up the desired phase. Because the chirp rate is the second derivative of the phase, faster chirps are, in a sense easier, realizable with only a single pass through the phase modulator. With our 4 GHz (8 GSample/s) AWG, we are able to chirp 5 GHz in 2 ns in a single pass. This chirp rate is a factor of ~50x higher than that used in our recent experiments.

Controlling the time evolution of the phase (or frequency), as discussed above, is one key aspect of coherent control. The other is controlling the amplitude. We take advantage of the same telecommunications technology and use a fiber-based electro-optic intensity modulator for this purpose. Using our 4 GHz AWG, we have recently realized pulse widths down to 0.15 ns. This is two orders of magnitude faster than the pulses used in our recent experiment and puts us well below the typical time scale (e.g., 20 ns) for spontaneous emission. Although our AWG has only a single output channel, we are able to drive both the phase and intensity modulators using an rf delay line and rf switches.

The phase and amplitude modulators have power limitations, due to photorefractive damage, at our 780 nm wavelength. To provide shaped pulses with reasonable power, we incorporate a 2-watt semiconductor tapered amplifier in a unique delayed double-pass configuration, realizing an overall gain of ~28 dB and a peak output power of several hundred mW.

Our combined ability to generate arbitrary frequencies (with the phase modulator) and amplitudes (with the intensity modulator) offers complete control over the waveform within our bandwidth limitations. This situation is complimentary to pulse shaping in the femtosecond regime, where the short high-bandwidth pulses are dispersed and the manipulations of phase and amplitude are done in the frequency domain. In contrast, our control is performed in the time domain. Our chirp production maintains the temporal duration and peak intensity of the pulse while increasing its bandwidth. In the frequency-domain manipulations, the bandwidth is not increased, but the pulse is stretched in time and its peak intensity reduced.

Although our immediate application of these chirped pulses is to coherent control of ultracold molecules, they may be useful in other types of AMO experiments. The range of pulse widths available will allow excitation on timescales comparable to or shorter than typical spontaneous emission lifetimes, allowing the effects of decoherence or dissipation on coherent control to be studied.

In collaboration with the group of Svetlana Malinovskaya at Stevens Institute of Technology, we have performed calculations of Raman transfer in three-level and four-level systems induced by a single chirped pulse on the nanosecond timescale. We found that efficient transfer between the ground-state hyperfine levels of the Rb atom, separated by 3 GHz, can be achieved with chirp parameters which should be experimentally attainable. For properly chosen parameters, the four-level system (two excited states instead of one) behaves effectively like a three-level system, exhibiting efficient transfer between the two ground-state levels. Although the calculations were done for atoms, they can be adapted to describe the transfer of population between vibrational levels of an ultracold molecule.

With an eye towards experimental implementation, we incorporated these Raman transfer calculations into a genetic algorithm simulation in order to optimize the transfer in the presence of experimental constraints. In a typical simulation, we would fix the chirp and allow the differential evolution algorithm to find the optimal temporal variation of the intensity. The optimal pulse shape was somewhat surprising: a sequence of three short pulses occurring at various times during the chirp.

Publications:

"Population Inversion in Hyperfine States of Rb with a Single Nanosecond Chirped Pulse in the Framework of a Four-Level Atom," G. Liu, V. Zakharov, T. Collins, P. Gould, and S.A. Malinovskaya, Phys. Rev. A **89**, 041803(R) (2014).

"Enhancement of Ultracold Molecule Formation by Local Control in the Nanosecond Regime," J.L Carini, S. Kallush, R. Kosloff, and P.L. Gould, New J. Phys. **17**, 025008 (2015).

"Enhancement of Ultracold Molecule Formation Using Shaped Nanosecond Frequency Chirps," J.L Carini, S. Kallush, R. Kosloff, and P.L. Gould, Phys. Rev. Lett. **115**, 173003 (2015).

"Efficient Formation of Ultracold Molecules with Chirped Nanosecond Pulses," J.L Carini, S. Kallush, R. Kosloff, and P.L. Gould, J. Phys. Chem. A **120**, 3032 (2016).

"Nanosecond Pulse Shaping at 780 nm with Fiber-Based Electro-Optical Modulators and a Double-Pass Tapered Amplifier," C.E. Rogers III and P.L. Gould, Opt. Express **24**, 2596 (2016).