Ultra-Cold Molecule Production

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Abstract

The production of Ultra-cold molecules is a goal of many laboratories throughout the world. Here we are pursuing a unique technique that utilizes the kinematics of atomic and molecular collisions to achieve the goal of producing substantial numbers of sub Kelvin molecules confined in a trap. Here a trap is defined as an apparatus that spatially localizes, in a known location in the laboratory, a sample of molecules whose temperature is below one degree absolute Kelvin. Further, the storage time for the molecules must be sufficient to measure and possibly further cool the molecules. We utilize a technique unique to Sandia to form cold molecules from near mass degenerate collisions between atoms and molecules. This report describes the progress we have made using this novel technique and the further progress towards trapping molecules we have cooled.
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Introduction and Background

The observation of Bose-Einstein Condensation (BEC) in a gas of sodium atoms in 1995 revolutionized the field of atomic-molecular-optical physics (AMO). The experimental realization of BEC has lead to extraordinary advances in AMO physics such as atom lasers, atom interferometry, gravity gradiometers, and gas phase superconductors. BEC and the underlying experimental techniques have opened a new doorway to explore fundamental reactions and scattering among ultra-cold atoms, whose applications point to new advances in field like metrology, quantum computing, and others.

Extending this work to molecules is, however, not straightforward. The techniques that work to cool atoms do not work for cooling molecules. New techniques must be developed in order to cool molecules to ultra-cold temperatures, where these new phenomena can be explored. The most critical step for producing ultra-cold atoms is a process called “optical cooling”. Optical cooling relies on the simple electronic structure of atoms to provide a quasi ‘two-level’ optical transition. Without a two-level like transition, the optical cooling process quickly breaks down and fails to cool the atoms. Due to the complex electronic structure of molecules, optical cooling can not work. However, several methods have emerged to cool molecules sufficiently so that they may be trapped in an external electric or magnetic field. So far no method is general or particularly successful. To date specialized cases (photo-association of cold alkali atoms) have been demonstrated, but, no general approach has proved successful for assembling collections of ultra-cold molecules.

The successful preparation and confinement of ultra-cold atoms\(^1\) have resulted in Bose-Einstein condensates (BEC)\(^2-4\) as well as many related phenomena, including atom optics,\(^5\) ultralow energy collision science,\(^6-7\) and the enhanced optical clocks.\(^8\) Ultra-cold atom samples, with temperatures ranging from 1 \(\mu\)K to 100 \(\mu\)K, are prepared in a two-step process: resonant laser light absorption and re-emission results ‘radiation pressure’ cooling of atoms to less than 1mK. In this context, “cooling” is generally reserved for process that increases the phase space (distribution of velocities and spatial locations) density of the atoms, normally by selectively slowing (or eliminating) the particles higher velocity particles over those with lower velocities. Atoms can be held in a magneto-optical or similar trap at these temperatures, at which point the temperature can further be reduced, typically by evaporative cooling.\(^9\)

The science of ultra-cold molecules (versus atoms) offers a considerable expansion of the possible observable phenomena, and an even broader likely range of applications. However, the cooling and trapping of molecules is more difficult, and a general way is still sought. This is largely because the radiation pressure cooling that is found to work so well for alkali atoms does not work well for molecules because ‘two-level’ systems cannot be isolated in their complex molecular energy-level structures.

However, a number of methods for slowing or cooling have been demonstrated or proposed\(^10-25\) to accomplish the first step of producing molecules cold enough to be trapped and further cooled. These methods include photoassociation of ultra-cold atoms,\(^13-16\) adiabatic tuning of a Feshbach resonance in a cold atomic gas,\(^17,18\) and buffer gas loading.\(^19-20\) In the latter approach, molecules are launched into a cold He buffer gas by laser ablation of a surface. The collisions with the He gas then cool the molecules in an anti-Helmholtz magnetic trap equilibrated at \(\sim 1\) Kelvin. Dipolar molecules which have significant ground-state Stark shifts have been slowed to a stop using Stark deceleration\(^21\). Another technique which has been proposed for slowing molecules is a spinning molecular beam source in which the velocity of the
spinning source cancels the velocity of the molecules flowing through it. While successful in cooling molecules, each approach has limitations in applicability or execution.

Recently we have pioneered a technique of single collision cooling of a molecule. By controlling the collision geometry and energy in a cross beam apparatus we have shown that the energy transfer in atom-molecule collisions can be exploited cool on the order of $10^6$ molecules into the milli-Kelvin temperature range. We have demonstrated this technique on collisions of NO and Ar producing NO between 40 and 400 milli-Kelvin in temperature. Our analysis of the experiment indicates that by careful picking of the masses of the collision partners this temperature range can be substantially decreased. Optimum cooling is obtained when the molecules are of the same mass and the quantum state that will cool the best is the one that is present in the molecular beam, the ground state. Elastic collisions cause molecules to stop when the masses are equal.

**Collisional Arrest of Molecules in Crossed Molecular Beams**

We recently reported our observations of a cooling process for molecules that relies upon a single collision between the molecule and an atom in a crossed molecular beam apparatus, producing molecules with a laboratory velocity that is nominally zero. The technique relies on a kinematic collapse of the laboratory velocity distribution of molecules that are scattered with a particular recoil velocity vector in the center-of-mass frame. The method depends on the fact that in binary collisions one of the collision partners can have a final center-of-mass-frame velocity that is essentially equal in magnitude and opposite in direction to the velocity of the center-of-mass, thus yielding a laboratory-frame velocity that is nearly zero. Cooling occurs because the center-of-mass velocity scales with initial NO velocity almost the same as the recoil velocity does.

Only collisions that result in NO molecules recoiling opposite to the direction of the motion of the center-of-mass experience the kinematic collapse. NO molecules recoiling in other directions have much larger laboratory velocities and quickly leave the scattering center. Therefore, only the NO molecules that have had their velocity distribution narrowed by collision remain in the region near the crossing point of the molecular beams.

This cooling process is very general, relying only on the experimentally selectable energy and momenta of the collision pair and not on any particular physical property of the colliding species. It is also realizable under easily accessible experimental conditions in crossed atomic and molecular beams. Further, this technique can be used to prepare a single, selectable ro-vibronic quantum state for trapping. We demonstrated this technique using an existing crossed molecular beam experimental apparatus that is not specifically optimized for the production of cold molecules. Inelastic collisions were observed between NO molecules in one beam and Ar in the other, specifically $\text{NO}(^2\Pi_{1/2}, j=0.5) + \text{Ar} \rightarrow \text{NO}(^2\Pi_{1/2}, j'=7.5) + \text{Ar}$.

Because of the mismatch of the masses of NO and Ar it is an inelastic collision that slows molecules. However if the masses of the collision partners are equal then the stopping collision is an elastic one. Examples of such partners are He collision with D$_2$ and ND$_3$ collision with Ne. As elastic collisions of molecules from molecular beams will produce cold ground state molecules this is an attractive technique.
Preliminary Results

We have previously used a crossed molecular beam experimental apparatus to measure the differential cross section of the inelastically scattered NO molecules in NO + Ar collisions. A pair of doubly-skimmed pulsed free-jet expansions forms well collimated molecular beams that intersect at approximately 90°. One of the beams is pure Ar, the other a mixture of 5% NO in Ar, with NO molecules predominantly in the ground rovibrational state. The Velocity Mapped Ion Imaging technique is used to characterize the scattering distribution and density of scattered NO molecules. In this method, the elastically and inelastically scattered NO products are observed by quantum-state-selective ionization using (1+1') resonance-enhanced multiphoton ionization (REMPI) through the NO \((A^2\Sigma\leftarrow X^2\Pi)\) transition at 226.057 nm. The bandwidth of our excitation laser is sufficiently narrow to ensure that only those NO molecules in a selected J-state are excited to the \(A^2\Sigma\) state and subsequently ionized by a 266-nm photon. The ions are formed in an electrostatic lens system that focuses and directs them onto a microchannel plate detector with a phosphorescent screen. Images created on the detector are captured with a CCD camera. Spatial positions in this image reveal the velocities of the scattered NO molecules being detected, with the velocity given by the ratio of the displacement on the detector, measured from the beam crossing point, to the flight time of the ions from the laser/molecular beam intersection region to the detector, multiplied by an instrumental magnification factor.

A false-color image of NO\(_{6.5}\) from NO\((^2\Pi_{1/2},j=0.5) + \text{Ar} \rightarrow \text{NO}(^2\Pi_{1/2},j=6.5) + \text{Ar}\) is shown in Fig. 1. For this image the scattered NO\(_{6.5}\) lies on a circle with a radius corresponding to its center-of-mass recoil velocity, about 410 m s\(^{-1}\), associated with its share of the total relative collision energy of 5.73±0.20 kJ mol\(^{-1}\). This circle of possible velocities appears in the Figure as a circle with varying intensity near its perimeter. The center of the scattering circle is the origin of the center-of-mass coordinate system. This origin is translated with respect to the origin of the laboratory-frame coordinate system, which is the intersection of the NO and Ar beams, by a distance that corresponds to the velocity of the center-of-mass of the NO + Ar system. The NO molecular beam contains a small amount of NO\(_{6.5}\) not cooled in the expansion, which is seen as a small diagonal band of intensity intersecting the circle of scattered NO\(_{6.5}\) on the left side of the image at \(\theta=0°\). On the circle of scattered NO\(_{6.5}\) product, an intense and sharp peak is observed near the top of the circle (\(\theta=85.6°\) in the center-of-mass-frame coordinate system.) This peak is at the origin of the laboratory frame. This near-zero laboratory velocity arises from NO\(_{6.5}\) produced by scattering of NO\(_{6.5}\) from an argon atom. If the residual NO\(_{6.5}\) in the molecular beam is elastically scattered into this direction, it would have a faster velocity and not appear at this position in the velocity image.

We have analyzed our measurements of these collisionally arrested molecules in some detail. Analysis of the near-zero velocity distribution of the NO left in the collision region reveals an upper limit root-mean-square velocity of 15 m s\(^{-1}\). This distribution of NO velocities corresponds to a temperature of approximately 0.03 K. We find that scattering into the NO\(_{7.5}\) state provides the highest density. The probability that an atom-molecule collision will result in an NO molecule that is cooled is small. From an analysis of our experimental data we estimate that the probability of a molecule having a collision resulting in a velocity less than 15 m s\(^{-1}\) is approximately \(10^{-5}\). In a typical crossed molecular beam experiment collision frequencies of approximately \(10^{13}\) collisions per second can be achieved during a single molecular beam pulse.
lasting about 0.5 ms and contained in a crossed-beam volume of $\sim 10^{-4} \text{cm}^3$. We estimate that densities of $10^8$-$10^9$ NO molecules cm$^{-3}$ in this single ($^2\Pi_{1/2}, v', j'=7.5$) rovibrational quantum state have been achieved.

**Figure 1.** Velocity-mapped ion image for collisions between nitric oxide and argon, NO($^2\Pi_{1/2}, j=0.5$) + Ar $\rightarrow$ NO($^2\Pi_{1/2}, j'=6.5$) + Ar at a center-of-mass collision energy of $5.73\pm0.20$ kJ mol$^{-1}$. The intense spot at the top of the scattering sphere is the result of a collapse of the velocity spreads of the molecular beams for those molecules whose scattered velocity vector cancels the center-of-mass velocity of the collision pair.

**Figure 2.** Velocity-mapped ion image for collisions between ammonia and neon, NH$_3$(X,j=0) + Ne $\rightarrow$ NO(X,j'=3) + Ne at a center-of-mass collision energy of $4.3\pm0.50$ kJ mol$^{-1}$. The intense spot at the top of the scattering sphere is the result of a collapse of the velocity spreads of the molecular beams for those molecules whose scattered velocity vector cancels the center-of-mass velocity of the collision pair.

Here we report the extension of these experiments to the NH$_3$ + Ne system. Figure 2 shows an image obtained ionizing the J=2 level of NH$_3$ utilizing the B (1)-X(1) transition at 166.2 nm. The image shows a similar shape to the image of NO collision with Ar with the distinctive build up of intensity around the zero velocity in the laboratory frame of reference. Calculations indicate that the velocity distribution should be colder for the NH$_3$ than for the NO but we are at the limit of our velocity measurement capabilities using the Ion Imaging technique so we do not observe colder NH$_3$. 
Trapping of Molecules

Once the molecules have been sufficiently slowed, it becomes possible to trap them in a localized optical, electric, or magnetic field. From there, it is expected that the molecules can be evaporatively cooled into the micro-Kelvin or nano-Kelvin temperature range required for formation of Bose-Einstein or degenerate Fermi gas. Purely nonresonant optical trapping of molecules using, for example, crossed CW laser beams, is a very general approach that has been demonstrated for the formation of an atom BEC\textsuperscript{29}. This approach relies on the polarization of atoms and molecules in response to an electric field. In the presence of a laser field, molecules and atoms feel a force that is proportional to the laser intensity and polarizability of the molecules or atoms. For the correct choice of laser, this force can form a trap for the molecules and atoms. For instance a 5 W CW AR\textsuperscript{+} laser focused to a $1/e^2$ beam waist of 10 $\mu$m results in a trapping potential. The depth of the trap for various molecules and atoms of interest is shown in Table I.

<table>
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<tr>
<th>Molecule</th>
<th>Polarizability ($10^{-24}$ cm$^3$)</th>
<th>Trap Depth (Micro Kelvin)</th>
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<tr>
<td>H$_2$</td>
<td>0.78</td>
<td>75.0</td>
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<td>CO$_2$</td>
<td>2.67</td>
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<td>Ar</td>
<td>1.66</td>
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<td>Kr</td>
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<td>Xe</td>
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<td>acetone</td>
<td>10.11</td>
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<tr>
<td>NH$_3$</td>
<td>2.21</td>
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<td>Benzene</td>
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<td>Br$_2$</td>
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<td>Cl$_2$</td>
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<td>HCl</td>
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<td>H$_2$S</td>
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<td>NO</td>
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<tr>
<td>O$_2$</td>
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<td>Pentane</td>
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<tr>
<td>SO$_2$</td>
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<td>H$_2$O</td>
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<td>142.5</td>
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This table shows that it is difficult to make a deep trap utilizing a laser field and that the well depth for No and for NH$_3$ are comparable. We have purchased a 50-watt CO$_2$ laser in order to attempt to trap NH$_3$ molecules after collision with Ne atoms. A CO$_2$ laser has the advantage that it has more power than an Ar$^+$ laser and its focal volume is larger. For utilization with the crossed molecular beam arrangement this larger volume is a distinct advantage.
Overlapping in space crossing of the molecular beams, where the molecules have been cooled, with a static electric field trap offers the possibility of forming a deeper and larger trap that relies on the interaction between the molecules permanent dipole moment and the static electric field. For ammonia we estimate that for an electric field of 10 Kilovolts per cm we can obtain a well depth of approximately 250 mK. A schematic of the trap is shown in Figure 3.

If a significant amount of molecules can be trapped in their ground electronic and ro-vibrational states then one has the opportunity of evaporatively cooling them to lower temperature. We have built an electrostatic trap for this purpose that will allow us to both trap the molecules then resonantly laser ionize them and image them onto a position sensitive ion detector in order to determine or trapping capability. A schematic drawing of a prototype electrostatic trap is shown in Figure 3. In this case, molecules that exhibit a ground-state Stark splitting (such as NO or NH₃) with low-field seeking levels can be trapped. While this trap is less general than the optical trap, the trap depth can approach ~1 Kelvin for molecules such as ND₃. This design produces a trap volume that is on the order of the volume of the crossing volume of the molecular beams.
New Cooling Concept

In addition to the crossed molecular beam cooling apparatus that we have built and used to demonstrate collisional cooling of molecules there is another variation on this technique that we are in the process investigating. As the molecular beam of atoms is slowed down and its velocity distribution collapsed then collisions with this beam should produce colder molecules. In this new technique we form a sample of optically cooled Rubidium atoms (Mass 85 and 87) in a magneto-optical trap (MOT), then collide molecules of similar mass with the ultra-cold rubidium to produce ultra-cold molecules. One such molecule is DBr (mass 83) and $^{85}$RbD (mass 87). In principle, an elastic collision of a Rb atom with a DBr molecule can extract 97% of the translational energy from the DBr. If it has a translational temperature to start with of 50 kelvin then it can cool to 1 degree Kelvin and be trapped. The first few rotational states can cool even more as they can absorb the excess energy. If we can produce and extract slowly moving DBr molecules by collision in the crossed molecular beam apparatus with Kr (mass 84) then those molecules can be stopped in the Rb trap by the application of either a static electric field or a non-resonant laser field. This apparatus is being built in order to attempt this experiment.

Conclusions

We have proceeded in several areas to create cold molecules. We have first optimized the scattering dynamics existing experiment to create a high concentration of cold NO molecules. We have obtained a 50 watt CO$_2$ laser for the off resonant laser trapping of molecules. We have extended our collisional studies to the system NH$_3$ +Ne and we have built a new apparatus for the production of ultra cold atoms as collision partners for molecules. Our initial focus will be to observe trapped NH$_3$ molecules, for which this laser arrangement produces an optical trap depth of 0.3 mK. We calculate that we can make a distribution of NH$_3$ with approximately 30 mK without trapping. We will observe the trapped molecules utilizing the existing ion-imaging detection scheme on our current apparatus. Observations of trap lifetime and temperature (by releasing the trap and observing the velocity distribution) will also be made. Modulating the laser and electric fields to achieve evaporative cooling, as well as trapping other molecules will be explored.
References

11. F. Masnou-Seeuws, P. Pillet in *Advances in Atomic, Molecular, and Optical Physics*, 47, 52.
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