The kinematic cooling of molecules with laser-cooled atoms

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Abstract. We propose a new scheme for the production of milli-Kelvin molecules via kinematic cooling through collisions with atoms in a magneto-optical trap (MOT). We will discuss the kinematic conditions necessary for producing cold molecules, the limits of the final attainable temperatures and the experimental implementation of this technique. Finally, we will look at some specific physical systems and discuss the effectiveness of kinematic cooling inside a MOT.

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1. Introduction

The cooling of molecules to sub-Kelvin temperatures promises to have a great impact on the fields of chemistry and physics. At these temperatures, the molecules are moving much more slowly in the laboratory reference frame compared to typical molecular beam velocities, leading to significantly longer observation times. At these low kinetic energies, strong external

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electric, magnetic, or optical fields may be used to trap, store and manipulate the molecules, making them ideal targets for studying collisional events as well as potential candidates for evaporative cooling to even lower temperatures. The ability to confine and control the molecules along with the extended observation times allows for ultra-high resolution spectroscopy that, for example, may enable the direct counting of the density of states of the molecules [1], as well as precision measurements of fundamental physical constants [2]–[4], or the detection of gravitational waves [5]. By trapping and orienting molecules prior to photo-dissociation, the spatial averaging associated with randomly oriented molecules can be greatly reduced, yielding new details in the observed angular distributions of the photofragments that can reveal the underlying dynamics of the photo-dissociation process [6]. Another consequence of the slow molecular velocities at these low temperatures is the increase in the deBroglie wavelength associated with the molecules. In analogy to atom optics, the wave-like properties of the cold molecules can be exploited to perform unique interferometric studies with molecules, such as the separation of mixtures of clusters by diffraction through a transmission grating [7]–[11].

There are two general strategies for making cold molecular samples: welding together pre-cooled atoms into diatomic molecules, and direct slowing or cooling of a molecular beam. The predominant techniques used to create cold molecules from cold atoms are photoassociation [12]–[15] and Feschbach resonance association [16]–[19]. Photoassociation of atoms consists of optical excitation of the unbound atoms to a bound, long-range electronically excited molecular state, followed by either Frank–Condon emission from that excited state to bound levels of the ground electronic state, or laser stimulation from the excited state to a particular ground vibrational state. In Feshbach resonance association, magnetic fields are used to tune the energy of a colliding pair of atoms in coincidence with a bound singlet state of the diatomic molecule. The primary advantage to welding together pre-cooled atoms is that the molecules formed are born translationally cold, typically in the micro-Kelvin temperature range. However, the molecules are formed in highly vibrationally excited states that can rapidly quench, although recent experimental advances [20]–[22] have utilized optical pumping schemes to transfer molecules to more deeply bound states, including the absolute ground state. These techniques apply only to diatomic molecules that are comprised of a small selection of atoms that can be laser cooled.

There are many techniques available for generating cold molecules by direct slowing or cooling of faster moving molecules. In these experiments, the molecules are typically injected into a high-vacuum region using a molecular beam valve. The supersonic expansion of the molecules into the vacuum region cools them down to their ground vibrational state with a rotational distribution of a few degrees Kelvin. While the internal degrees of freedom are cooled by the expansion, the molecules are left translationally hot, moving at supersonic velocities in one dimension. The goal of the direct cooling/slowing is to remove this translational energy and bring the molecules to rest in the laboratory reference frame. Direct slowing of molecules has the advantage that a larger variety of diatomic and complex molecules may be cooled.

One conceptually straightforward technique for slowing down molecules in a supersonic beam is to move the molecular beam valve backwards in the laboratory reference frame with a velocity equal and opposite to that of the escaping molecular beam [23], canceling out the translational velocity in the laboratory frame. Other techniques fall broadly into three categories: using external electric or magnetic fields, using optical fields or using collisions. Both Stark deceleration [24, 25] and Zeeman deceleration [26, 27] have demonstrated the successful
production of samples of cold atoms and molecules using external electric and magnetic fields, respectively. Optical field techniques include the use of far off-resonance laser beams for optical Stark deceleration [28] and the production of very polarizable molecular Rydberg states [29] that can be easily slowed with electric fields. Collisional techniques capable of producing molecules at sub-Kelvin temperatures include bulk cooling using 300 mK helium gas as a collision partner [30], the entire field of trapping molecules in superfluidic helium clusters [31]–[33], and kinematic cooling. In kinematic cooling, molecules undergo single collisions with atoms such that a subset of the molecules are left moving slowly in the laboratory reference frame [34]. It is so called because the amount of cooling is strictly determined by the kinematics of the collision. The possibility of creating a cooled molecule as the product of a reactive scattering event has also been investigated [35, 36]. These techniques have produced samples of molecules in the milli-Kelvin temperature range at densities that are too low to be considered ultracold.

Here we present a novel technique based on kinematic cooling physics, which offers greater experimental simplicity than the current kinematic cooling technique. In conventional kinematic cooling, supersonic molecules in a molecular beam are cooled to milli-Kelvin temperatures by either elastic [37] or inelastic [38] collisions with an atomic beam intersecting at a near 90° angle. Recent experiments [38] have shown that secondary collisions between the cooled atoms and the remnants of the parent atomic and molecular beams can reheat and destroy the cold molecule sample. Here we propose replacing the target supersonic atomic beam with a dense cloud of pre-cooled atoms in a magneto-optical trap (MOT). This seemingly minor change alters the kinematic equations governing the cooling process, affecting the experimental geometry and allowing for a surprisingly large number of molecules to be cooled to sub-Kelvin temperatures via elastic scattering. Further, secondary elastic collisions with the atoms would no longer collisionally reheat the cold molecular sample, but rather serve to further cool the molecules.

2. Discussion

The physics behind this novel cooling approach can be summed up in the behavior of a Newton’s cradle device. Consider a Newton’s cradle with two balls of equal mass; one ball is initially stationary while the second gets pulled and released. As the second ball strikes the first head on, all of the kinetic energy from the second ball is transferred to the first, bringing the second ball to rest. This is analogous to the kinematic cooling process, wherein a ‘hot’ molecule collides with a near stationary atom of similar mass, ejecting the atom and bringing the molecule to rest. The difference is that in the Newton’s cradle, the balls have equal mass and are constrained to collide with a zero impact parameter. To generalize this to molecules colliding with laser cooled atoms, we must analyze the collision between these particles for arbitrary masses and nonzero impact parameters.

The collisional process can be characterized by the amount of energy transferred from one particle to another, which we calculate by modeling the colliding particles as hard spheres. Consider two particles: particle A with mass $m_A$ and velocity $v_A$, and particle B with mass $m_B$ and velocity $v_B$. Figure 1 shows the relationship between the velocity $v_A$ of particle A in the laboratory frame of reference and the velocity $u_A$ in the center-of-mass (COM) reference frame. Primed and unprimed vectors refer to post- and pre-collision velocities, respectively. After the collision, the particle scatters onto a sphere in velocity space (dictated by conservation of energy and momentum) around the COM of the system, which moves with velocity

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Figure 1. Vector diagrams of the pre- and post-collision velocities for a hard sphere collision between two particles with equal masses. Initially, particle A has velocity \( v_A \) and particle B is at rest in the laboratory frame (lab frame velocities are designated by \( \vec{v} \)).

\[
\vec{v}_{\text{COM}} \equiv \left[ m_A \vec{v}_A + m_B \vec{v}_B \right] / (m_A + m_B) \text{ in the laboratory reference frame.}
\]
The scattering angle \( \chi \) is determined by the impact parameter of the collision.

For elastic scattering, \( u_A = u_A' \), and the product velocity vectors have the following relationship:

\[
(v_A')^2 = (u_A')^2 + (v_{\text{COM}})^2 - 2 \cos(\pi - \chi) \cdot v_{\text{COM}} \cdot u_A'.
\]

Assuming particle B is initially at rest \( (\vec{v}_B = 0) \), the scattering angle in the COM frame is given by

\[
\cos \chi = \left[ (v_A'/v_A)^2 - (m_A^2 + m_B^2)/(m_A + m_B)^2 \right] / [2 \mu_{AB} / (m_A + m_B)],
\]

where \( \mu_{AB} \) is the reduced mass of the system. For equal masses, this reduces to \( \cos \chi = 2(v_A'/v_A)^2 - 1 \). We see that the post-collision velocity of particle A in the laboratory frame is minimized for large scattering angles.

In the COM frame, half of the velocity is in A and half is in B (COM velocities are designated by \( u \)). After the elastic collision, conservation of energy and momentum require that the final velocities of A and B (designated as primed) lie on a sphere in velocity space as shown above where \( |u_A'| = |u_B'| = |v_A'| = |v_B'| \). The intersection between the sphere and lab
Figure 2. Dynamics of two-particle hard sphere scattering. The COM frame scattering angle is given by $\chi$ and $\alpha$ is the angle subtended by the radius to the impact point and the perpendicular to the center line of the collision. The impact parameter is given by $b$ and $d$ is the sum of the radii of the two spheres.

Frame origin corresponds to the case where $v'_A = 0$. In the laboratory frame the particles A and B are scattered at $90^\circ$.

Figure 2 shows the relationship between the scattering angle and impact parameter of the collision

$$b = IB = d \cos(\alpha) = d \cos(\chi/2),$$

where $d = R_A + R_B$ is the distance of minimum approach between the COMs of the two spheres. From this one-to-one correspondence between the angle of scattering and the impact parameter we see that the post-collision velocity of particle A is minimized for small impact parameters. This is expected, as for a head-on collision $b = 0$ and $\chi = \pi$ resulting in direct recoil, whereas for $b = d$ and $\chi = 0$ no deflection is expected.

To determine the number of cold molecules that can be generated using this kinematic cooling technique, we first need to find the partial differential cross-section $\sigma_{p(\min)}$ for collisions resulting in a minimum scattering angle $\chi_{\min}$, from which we can calculate the fraction of collisions, $F \equiv \sigma_{p(\min)}/\sigma_T$, that cool the molecules down to the corresponding maximum final velocity. The partial differential cross-section is determined by summing contributions from impact parameters between zero and $b_{\min}$

$$\sigma_{p(\min)} = \int_0^{2\pi} \int_0^{b_{\min}} b \, db \, d\phi = \pi \, d^2 \cos^2 \left( \frac{\chi_{\min}}{2} \right) = \pi \, d^2 \left( \cos \chi_{\min} + 1 \right) / 2,$$

while the total cross-section of all collisions is given by the total area of the collision,

$$\sigma_T = \int_0^{2\pi} \int_0^d b \, db \, d\phi = \pi \, d^2.$$

The fraction of collisions having $\chi \geq \chi_{\min}$ is therefore $F \equiv \sigma_{p(\min)}/\sigma_T = 1/2(\cos \chi_{\min} + 1)$. Substituting in equation (2) gives

$$F = \frac{1}{2}\left\{ \left[ (v'_A/v_A)^2 - (m_A^2 + m_B^2)/(m_A + m_B)^2 \right]/[2\mu_{AB}/(m_A + m_B)] + 1 \right\}.$$
Using the fact that \( \frac{v_A^2}{v_A^2} = \frac{E_A'}{E_A} \) this fraction can be expressed in terms of the initial \( E_A \) and post-collision \( E_A' \) energies of particle A, \[
F = \frac{1}{2} \left[ \frac{E_A'}{E_A} - \left( m_A^2 + m_B^2 \right) / \left( m_A + m_B \right)^2 \right] / \left[ 2 \mu_{AB} / \left( m_A + m_B \right) \right] + 1. \tag{7}
\]
In the case of degenerate masses \( m_A = m_B \), this equation reduces further to \[
F = E_A'/E_A. \tag{8}
\]
This simple result gives the fraction of collisions between hard spheres of equal mass that transfers a particular amount of energy, where particle B is assumed to be initially at rest \( (v_B = 0) \). Thus, if we require at least half of particle A’s initial energy to be transferred to the previously stationary particle B \( (E_A' = 0.5E_A) \), then the fraction of collisions satisfying this condition is also a half. If we want to have a collision that transfers at least 99% of the energy to particle B, then \( E_A' = 0.01E_A \) and \( F = 0.01 \), so 1% of the random hard sphere collisions will accomplish this. For unequal masses, the fraction of contributing collisions decreases by a factor of two when the mismatch of masses exceeds 15%. As a result, this process is capable of slowing a large variety of molecules even for a single target species of atom in the MOT.

The density of cold molecules we expect to achieve with this technique is determined by the density of atoms in the MOT and the fractional energy that needs to be removed from the molecules. At steady state, the rate of production of cold molecules resulting from collisions between thermal molecules and cold atoms is equal to the loss rate due to collisions between the cold molecules and the incoming thermal molecules. We assume that the total cross-section for molecule–atom collisions is the same as for molecule–molecule collisions; however, only a small fraction \( F \equiv \sigma_P / \sigma_T \) of the molecule–atom collisions results in cold molecules with sufficiently slow velocities in the laboratory frame. Since the rate of collisions is proportional to the density of the particles involved, the density of atoms \( n_{\text{atom}} \) and molecules \( n_{\text{mol}} \) are related as \[
\begin{align*}
n_{\text{mol}} &= F \cdot n_{\text{atom}}. \tag{9}
\end{align*}
\]
For example, if the fraction of collisions that sufficiently cool a molecule below a certain temperature is \( F = 10^{-3} \), then a cold molecule will have an equal probability of being generated or lost when the density of molecules is \( 10^{-3} \) that of the atoms. Note that slower initial molecular velocities and higher atom densities in the MOT will increase the number of cold molecules available when steady state is achieved.

This assumes that the main loss mechanism from the trap is collisions with the background molecular gas. If, on the other hand, the density of the background molecular gas is too high, then the equilibrium MOT density \( n_{\text{atom}} \) will decrease, leading to the formation of fewer cold molecules. In the case where the loss rate of both the cold molecules and the MOT are due exclusively to collisions with the thermal molecules and other background atoms, the equilibrium density of cold molecules becomes \[
\begin{align*}
n_{\text{mol}} &= F \cdot n_{\text{MOT}} \cdot \frac{\beta}{(1 + \beta)^2}, \tag{10}
\end{align*}
\]
where \( n_{\text{MOT}} \) is the MOT density in the absence of the additional thermal background of molecules, and \( \beta = n_{\text{thermal}} / n_{\text{bg}} \) is the ratio of thermal molecules \( (n_{\text{thermal}}) \) to other background atoms \( (n_{\text{bg}}) \). This has a maximum of \( n_{\text{mol}} = F \cdot n_{\text{MOT}} / 4 \), when \( \beta = 1 \) or \( n_{\text{thermal}} = n_{\text{bg}} \). In general, however, the loss rate for the MOT is dominated by other sources, such that the thermal molecule density can be increased relative to that of the other background gases without significantly
impacting the MOT. In this regime, the density of cold molecules will be much closer to $n_{\text{mol}} = F \cdot n_{\text{MOT}}$.

This cooling technique has many advantages over other collisional cooling techniques. Unlike buffer gas cooling [12] where the large mass mismatch requires the molecules to undergo many collisions to be cooled, this technique relies on single collisions, and therefore does not require having favorable elastic to inelastic scattering cross-section ratios. At typical MOT densities, multiple cooling collisions between disparate mass particles are highly unlikely to occur. Also, in contrast to previous conventional kinematic cooling experiments [39], this technique utilizes elastic collisions and is more efficient for slower initial velocities. Another consequence of using cold atoms as the collisional targets rather than a supersonic atomic beam is that it relaxes the experimental requirement of the $90^\circ$ scattering geometry, eliminating the need for a well-collimated molecular beam source. This allows for experimental simplifications and, as we will discuss below, for much lower temperatures to be achieved.

3. Experiment

The usefulness of any cooling method is largely determined by the total number of trappable molecules that it can generate. In the case of kinematic cooling with laser-cooled atoms, we begin with a continuously loaded atomic MOT, into which we introduce a molecular gas with the same or similar mass to the atoms in the trap. The ideal molecular source is one that is both translationally and rotationally cold, and has a high flux. A molecular beam provides a source of rotationally and vibrationally cold molecules, but because they are moving at supersonic speeds, the fraction of collisions removing enough kinetic energy to trap the molecules is relatively small. This fraction could be greatly increased by employing more conventional slowing techniques to achieve a lower initial velocity, but at the expense of added complexity. Alternatively, we can consider bleeding the gas of interest into the chamber, which allows for slower initial velocities and consequently colder final temperatures, as well as a much simpler set up. Because these molecules have a thermal distribution of internal rotational and vibrational states, only a fraction of the cold molecules formed will be in the rotational ground state, and secondary collisions between the rotationally excited molecules and the cold atoms can expel them from the trap. This will reduce the total number of trappable cold molecules at equilibrium; however, the post-collision rotational state distribution itself may provide information about rotational energy transfer and chemical dynamics.

For simplicity, we consider here the case of bleeding in a background gas of the desired molecule. If the background pressure is low enough not to overwhelm the loading rate of the atomic MOT, then the system will reach equilibrium with some steady state production rate of slow molecules. By superimposing an appropriate molecular trap over the MOT region, we can confine and collect the cold molecules that are generated with energies less than the molecular trap depth. For typical systems, the upper limit of the trappable velocity distribution corresponds to molecular temperatures below 500 mK but greater than 100 mK. Since the cooling efficiency is tied to the relative masses of the colliding particles, we will consider both a mass resonant system and a system with non-equal masses in evaluating the utility of the kinematic cooling technique.

As an example of a mass-resonant system, we consider the scattering of rubidium deuteride ($\text{D}^{85}\text{Rb}$) molecules off of rubidium 87 ($\text{^{87}Rb}$) atoms collected in a MOT. The cooled $\text{D}^{85}\text{Rb}$
molecules are to be confined by an optical dipole trap superimposed on the MOT region. The $^{87}$Rb MOT is loaded with a typical density of around $10^{10}$ atoms per cc, and a background of room temperature (300 K) $^{85}$Rb molecules ($v_A = 170$ m s$^{-1}$) is introduced. If we require a final velocity of $v'_A \sim 14$ m s$^{-1}$ (1 K), we find that $\sim 6.7 \times 10^{-3}$ of the collisions produce a $^{85}$Rb molecule in this temperature range, giving a steady state density of approximately $6 \times 10^7$ molecules at sub-Kelvin temperatures. According to equation (6), $\sim 10^{-5}$ of the collisions cool the $^{85}$Rb to 10 mK or less, yielding an estimated $10^5$ molecules per cc in the milli-Kelvin temperature range. Because of the overlap between the MOT and molecular trap, if the collisional losses are favorable, the trapped cold molecules will undergo thermalizing collisions with the $^{87}$Rb atoms, which are at a temperature of $\sim 100$ $\mu$K [40]. These results are for the most probable velocity in the thermal distribution of the $^{85}$Rb.

We now turn to a molecule–atom system with a slight mismatch in the particle masses. In the case of deuterated hydrogen bromide ($^{D81}$Br) scattering off of rubidium 85 ($^{85}$Rb), the initial conditions are similar to that of $^{D85}$Rb and $^{87}$Rb, except that $m_A < m_B$. For the non-mass-resonant system, a single collision cannot bring the molecule to rest in the laboratory frame, and there is a minimum velocity beyond which a molecule cannot be cooled. For example, given a mass ratio of 83–85, we find that $\sim 3 \times 10^{-3}$ of the collisions can produce $^{D81}$Br with a final temperature of 1 K or less; however, no elastic collisions can cool $^{D81}$Br from an initial velocity of 170 m s$^{-1}$ down to temperatures of less than 10 mK. Fortunately, as illustrated in figure 3(a), lowering the initial velocity of the incoming molecules also lowers the minimum obtainable post-collision temperature. If $^{D81}$Br is cooled to liquid nitrogen temperatures (90 m s$^{-1}$), the decrease in the initial velocity shifts the minimum obtainable temperature to a few milli-Kelvin.

Figure 3(b) shows the velocity distribution for a room temperature sample of $^{D81}$Br, and a sample cooled to liquid nitrogen temperatures. Note that in either case, the lower end of the thermal Boltzmann distribution will cool more efficiently to even lower temperatures.

**Figure 3.** The left-hand figure shows the post-collision fraction and final temperature for selected initial velocities for $^{D81}$Br scattering off of $^{85}$Rb. The right-hand figure shows two Boltzmann distributions; the dashed line corresponds to $^{D81}$Br at liquid nitrogen temperatures, the solid line is a room temperature distribution, and the vertical line is approximately the temperature of $^{D81}$Br supersonically expanded in a xenon carrier gas in a molecular beam.
The ability to use an effusive or thermal molecular source lets this cooling technique take advantage of lower impact velocities, allowing it to cool molecules to very low temperatures even with significant mass differences. For experiments where the thermal rotational state distribution of the molecules presents a problem, using this technique in conjunction with other molecular beam cooling techniques such as the counter-rotating nozzle [23] has promise to create samples of cold molecules in an experimentally simple and low-cost apparatus. It should be noted that in this discussion we have neglected the effects of inelastic collisions with either ground or electronically excited $^{87}$Rb on the density of cold molecules that can be formed. These inelastic collisions with electronically excited $^{87}$Rb are very exothermic and detrimental to the cooling process but can be greatly reduced by using, for example, a dark-spot MOT [41]. We have also assumed that chemical reactions between the molecules and atoms that can readily eject molecules from the trap are negligible.

4. Conclusion

We have proposed a novel variation of the kinematic cooling technique for generating samples of milli-Kelvin temperature molecules. Because the kinematic technique only relies on a single collision, molecules can be cooled even with an unfavorable ratio of elastic to inelastic collision cross-sections. We have shown that for a test system of $^{85}$Rb scattering off of $^{87}$Rb, we can expect to produce $\sim 10^5$ mK molecules per cc from a room temperature vapor, and even larger numbers if the initial molecular velocities are reduced. Similarly, for $^{81}$Br scattering from $^{85}$Rb we calculate that we may be able to produce $\sim 10^6$ molecules per cc at milli-Kelvin temperatures assuming we can start with $^{81}$Br cooled to liquid nitrogen temperatures. As the milli-Kelvin molecules are trapped coincident with the micro-Kelvin temperature atoms, further collisional cooling may occur, offering the possibility of samples of ground state molecules at micro-Kelvin temperatures.

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