

Ion-Atom Cold Collisions and Atomic Clocks

John D. Prestage, Lute Maleki, and Robert L. Tjoelker
Jet Propulsion Laboratory, Pasadena, CA

Introduction

Collisions between ultracold neutral atoms has for some time been the subject of investigation, initially with hydrogen and more recently with laser cooled alkali atoms [1]. Advances in laser cooling and trapping of neutral atoms in a magneto-optic trap (MOT) have made cold atoms available as the starting point for many laser cooled atomic physics investigations. The most spectacularly successful of these, the observation of Bose-Einstein condensation (BEC) in a dilute ultra-cold spin polarized atomic vapor [2], has accelerated the study of cold collisions. Experimental and theoretical studies of BEC and the long range interaction between cold alkali atoms is at the boundary of atomic and low temperature physics. Such studies have been difficult and would not have been possible without the development and advancement of laser cooling and trapping of neutral atoms. By contrast, ion-atom interactions at low temperature, also very difficult to study prior to modern day laser cooling, have remained largely unexplored. But now, many laboratories worldwide have almost routine access to cold neutral atoms. The combined technologies of ion trapping, together with laser cooling of neutrals has made these studies experimentally feasible and several very important, novel applications might come out of such investigations.

This paper is an investigation of ion-atom interactions in the cold and ultra-cold temperature regime. Some of the collisional ion-atom interactions present at room temperature are very much reduced in the low temperature regime. Reaction rates for charge transfer between unlike atoms, $A + B^+ \rightarrow A^+ + B$, are expected to fall rapidly with temperature, approximately as $T^{5/2}$. Thus, cold mixtures of atoms and ions are expected to coexist for very long times, unlike room temperature mixtures of the same ion-atom combination. Thus, it seems feasible to cool ions via collisions with laser cooled atoms.

Many of the conventional collisional interactions, exploited as a useful tool at room temperature and higher, are greatly enhanced at low energy. For example, collisional spin transfer from one species of polarized atoms to another has long been a useful method for polarizing a sample of atoms where no other means was available. Because optical pumping cannot be used to polarize the nuclear spin of ^{129}Xe or ^3He [3] (for use in nmr imaging of the lungs), the nuclear spins are polarized via collisions with an optically pumped Rb vapor in a cell containing both gases. In another case, a spin polarized thermal Cs beam was used [4] to polarize the hyperfine states of trapped $^3\text{He}^+$ ions in order to measure their hyperfine clock transition frequency. The absence of an x-ray light source to optically pump the ground state of the $^3\text{He}^+$ ion necessitated this alternative state preparation. Similarly, Cd^+ and Sr^+ ions were spin-oriented via collisions in a cell with optically pumped Rb vapor. Resonant rf spin changing transitions in the ground state of the ions were detected by changes in the Rb resonance light absorption [5].

Because cold collision spin exchange rates scale with temperature as $T^{-1/2}$ this technique is expected to be a far more powerful tool than the room temperature counterpart. This factor of

100 or more enhancement in spin exchange reaction rates at low temperatures is the basis for a novel trapped ion clock where laser cooled neutrals will cool, state select and monitor the ion clock transition. The advantage over conventional direct laser cooling of trapped ions is that the very expensive and cumbersome uv laser light sources, required to excite the ionic cooling transition, are effectively replaced by simple diode lasers.

Review of Low Temperature Ion-Atom Collisions

The following sections will summarize the expected low temperature reaction rates for various processes to be investigated in the proposed work,

Long Range Ion-Atom Interactions

The cold and ultra-cold collisions to be studied in this work have not been experimentally accessible until just recently following the proliferation of laser cooled neutral vapors. Cross-sections for collision processes between ions and atoms at these energies can be estimated both classically and quantum-mechanically. One such classical cross-section is the impact collision of an ion and atom drawn together by their polarization induced attraction, written $V_{\text{pol}}(r) = -\alpha e^2/2r^4$ where α is the electric polarizability of the neutral atom. The two body classical orbit problem is reduced to an equivalent problem of a single particle of reduced mass μ ($1/\mu = 1/M + 1/M_{\text{neutral}}$) in the attractive ion-neutral interaction $V_{\text{pol}}(r) = -\alpha e^2/2r^4 = -C_4/r^4$ and the repulsive angular momentum barrier $V_{\text{eff}}(r) = L(L+1)\hbar_{\text{bar}}^2/2\mu r^2$ where L is the angular momentum quantum number. An atom with sufficiently small impact parameter will be drawn to an ion and impact will occur. This sort of collision [6] occurs with

cross-section $\sigma \approx \pi \alpha_0^2 \sqrt{C_4'/E}$ where the kinetic energy of the particles, E, is

in atomic units $e^2/a_0 = 27.2 \text{ eV}$ and $C_4 = C_4'(e^2/2a_0)a_0^4$. For 1 K ion atom temperatures, impact cross-sections are $\sim 10\text{-}12 \text{ cm}^2$ and increasing as T-in as the collision temperatures diminish. However, the reaction rate, $\langle \sigma v \rangle$, is independent of temperature for C_4/r^4 ion-atom potentials. Though classical, this model shows that at low collision energies the angular momentum barrier is weak and particles at large impact parameters will fall together.

Collisional Cooling of Trapped Ions

Collisional cooling between a laser cooled beam of atoms or cold atoms in a MOT should be straight forward. The energy loss per collision $\delta E/E$ for ions of mass M initially at room temperature colliding with laser cooled neutrals of mass m is $\delta E/E = m/M$. The cross-section for ion-atom interactions at room temperature can be estimated from the impact model at about $6 \times 10^{15} \text{ cm}^2$. Assuming Li as the laser cooled gas of density $10^{10}/\text{cm}^3$ [7], a collision rate of $n v \sigma \approx 60/\text{sec}$ yields an energy loss rate $1/E dE/dt \approx 2/\text{sec}$. Thus, a few seconds after the hot ion enters the cold neutral vapor it will have cooled to the cold neutral temperature.

Collisional cooling between a cold atom and an ion has never been experimentally investigated.

Ion-ion “sympathetic” cooling, where one species is laser cooled and the other is thermalized via collisional energy loss has been demonstrated[8]. In this work both types of ion were confined to a Penning trap and only momentum transfer interactions can occur because the like charges **repell** and close approach is impossible. By contrast, ion-neutral interactions are long range attractive and close approach is likely so that spin exchange interactions can occur with high probability as we describe later. However, with close approach there is the question of charge transfer between the cold alkali atom and ion during momentum and spin transfer collisions.

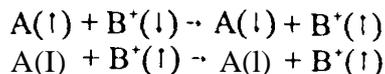
Charge Transfer in Cold Ion-Atom Collisions

Unlike impact collisions whose reaction rate is constant with falling temperature, inelastic charge transfer rates where the neutral loses its valence electron to the ion, should be drastically reduced at low temperature. The possibility of collisionally cooling a collection of trapped ions with cold neutrals would be remote should the ion be neutralized by the atom during the multiple collisions required to reach thermal equilibrium.

Charge transfer in ion-atom collisions[6] where the ion and atom are different atoms, eg., laser cooled Li atoms and trapped Hg^+ ions, is an inelastic collision. That is, a part of the translational kinetic energy of the colliding pair, AE , must be converted into internal energy in transferring the electron from an energy state in the Li atom to the nearest available energy state in the resulting neutral Hg atom. For Hg^+ colliding with the commonly used laser cooled alkali atoms, $AE \approx 0.1$ eV, many orders of magnitude larger than the cold collision energies attainable in this work. Charge transfer in these asymmetric collisions (unlike ion and atom) have been successfully modelled for collision energies higher than the low temperature domain to be studied in the work proposed here. The scaling to colder collisions for the asymmetric charge transfer follows the Massey adiabatic criterion, i.e., when $aAE/h_{\text{bar}}v \approx 1$ the inelastic cross-section is maximum, where a is an atomic size for the atoms in collision and v is the velocity at closest approach. The electron is able to absorb energy AE from the changing inter-atomic fields whose spectrum has its largest component around frequency $\omega \approx v/a \approx \Delta E/h_{\text{bar}}$. At lower velocities where $a\Delta E/h_{\text{bar}}v \gg 1$ the cross-section falls off rapidly with decreasing v [6] falling approximately as $(h_{\text{bar}}v/a\Delta E)^4$ and thus the reaction rate, $\langle \sigma v \rangle$, falls as $T^{5/2}$ with temperature. It would seem that charge transfer between unlike atoms would be very difficult at cold temperatures. We will return to this question in the next section.

Low Energy Spin Exchange Collisions

The electron spin exchange reaction between an alkali atom and an alkali-like ion, both in $^2S_{1/2}$ ground states [9] is written



The spin dependent interaction between atoms, $V(\mathbf{r}) = V_0(\mathbf{r}) + \mathbf{S}_A \cdot \mathbf{S}_B V_1(\mathbf{r})$, conserves total electron spin $S = \mathbf{S}_A + \mathbf{S}_B$ without any changes in orbital state. The inter-atomic potential is very

different for the $\uparrow\uparrow$ state where \mathbf{S}_A is parallel to \mathbf{S}_B than the $\downarrow\downarrow$ state where \mathbf{S}_A and \mathbf{S}_B are anti-parallel. A typical interaction energy vs internuclear separation is shown in Figure 1. The origin of this spin dependent interaction stems from the overall symmetry requirement of the electron wavefunction. The $\uparrow\uparrow$ state has a node of the electron wavefunction between the colliding atoms and thus the two positively charged nuclei are not screened from one another as in the state $\downarrow\downarrow$ where the electron wavefunction has its maximum value between the atoms. The shielding between the nuclei in this $\downarrow\downarrow$ state results in the binding of diatomic molecules and is several orders of magnitude stronger than the dipolar magnetic interaction of the electron spin magnetic moments.

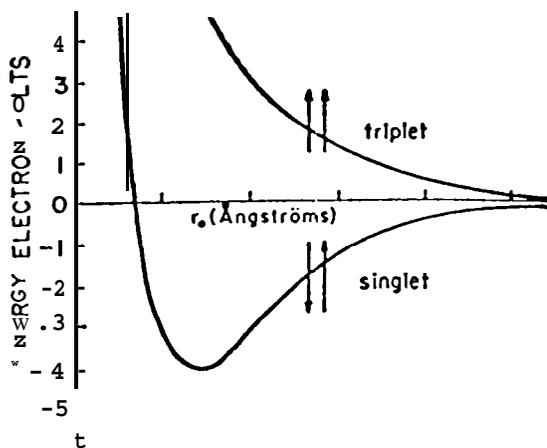


Figure 1: Interaction energy of two hydrogen atoms as a function of the internuclear separation r [ref. 9].

The quantum mechanical cross-section for spin exchange is given by

$$\sigma = \frac{\pi}{k^2} \sum_{l=0}^{l_{cutoff}} (2l+1) \sin^2(\delta_l^{\uparrow\uparrow} - \delta_l^{\downarrow\downarrow})$$

where $k = 2\pi/\lambda_{dB}$ and $\delta_l^{\uparrow\uparrow}$ and $\delta_l^{\downarrow\downarrow}$ are the phase shifts incurred in the scattering from the triplet and singlet inter-atomic potentials of Figure 1. For cold collisions where only a few partial waves contribute (see Table 1), the cross-section approaches $\pi \lambda_{dB}^2 = \pi a_0^2 82(\mu(\text{amu})E(^{\circ}\text{K}))^{-1}$ where μ is the reduced mass in amu of the collision partners and E is the kinetic energy in units of temperature $^{\circ}\text{K}$. Note that the rate constant, $\langle \sigma v \rangle$, for spin exchange collisions at low temperature increases as T^{-1} with decreasing temperature. For mK collision temperatures, cross-sections can be of order 10^{-12} cm^2 , two orders of magnitude higher than room temperature values.

With regard to charge transfer in the cold collision regime, ion-atom collision partners approaching one another in the singlet state $\downarrow\downarrow$ are drawn together gaining an eV or more of

energy (Figure 1), many orders of magnitude higher than their separated energy. Thus ion-atom collision speeds could satisfy the Massey criterion for these singlet state collision partners and readily charge transfer. By contrast, triplet state or spin parallel collision partners experience a repulsive exchange interaction so that $v/a \ll \Delta E/h_{\text{bar}}$ for all times preventing charge transfer. This could form the basis for state selection in the trapped ion cloud. That is, a spin polarized neutral beam will charge transfer and destroy the anti-parallel spin state ions without combining with the spin parallel ions. The remaining ion cloud would be spin aligned with the spin polarized neutral atoms. Externally driven rf spin flip transitions in the ion cloud would be followed, indeed, would be signalled by the generation of Li^+ ions, the byproduct of the charge transfer with the Hg^+ ion. Because charged particles can be detected with nearly 100% efficiency, the clock transition in the trapped ions could be monitored with very high SNR. This will be discussed more in the section on atomic clocks.

The Onset of Quantum S-wave Scattering

The long range interaction between an ion and neutral atom is via an induced electric dipole in the neutral resulting in an attractive interaction $V_{\text{pol}}(r) = -\alpha e^2/2r^4$ where α is the electric polarizability of the neutral, These measured values [10] are listed in Table 1 in units of a_0^3 , the cube of the Bohr radius. The attractive $V_{\text{pol}}(r) = -C_4/r^4$ and repulsive $V_{\text{eff}}(r) = L(L+1)h_{\text{bar}}^2/2\mu r^2$ together produce a maximum in the long range potential at $K(L) = (4\mu C_4/L(L+1)h_{\text{bar}}^2)^{1/2}$ of magnitude $V_c(L) = L(L+1)h_{\text{bar}}^2/4\mu R_c^2(L)$. Table 1 summarizes these values.

| | C_4^\dagger | $R_c(L=1)/a_0$ | $T_c = V_c(L=1)/k_B$ | $L_{\text{cutoff}} (T=1 \text{ mK})$ |
|--------------------|---------------|----------------|----------------------|--------------------------------------|
| Li + Hg^+ | 163 | 1430 | 6 μK | 3 |
| Na + Hg^+ | 158 | 2410 | 0.7 μK | 5 |
| K + Hg^+ | 291 | 4200 | 0.2 μK | 8 |
| Rb + Hg^+ | 317 | 5940 | 40 nK | 12 |
| Cs + Hg^+ | 400 | 7670 | 20 nK | |

In the table we have listed $C_4^\dagger = \alpha/a_0^3$ where $C_4 = C_4^\dagger(e^2/2a_0)a_0^4$, $a_0 = h_{\text{bar}}^2/me^2 = 0.529 \times 10^{-8} \text{ cm}$ and $e^2/2a_0 = 13.6 \text{ eV}$. In addition, $a_0^3 = 0.149 \times 10^{-24} \text{ cm}^3$.

For collision temperatures less than T_c , the angular momentum barrier prevents ion-atom distances closer than $R_c(L)$ except for $L = 0$, i.e., s-wave scattering. These barriers are somewhat weaker and occur at much greater inter-atom distances than the neutral-neutral $-C_6/r^6$ van der Waals induced barriers [1]. For ultracold collisions at T_c or less, only s-wave interactions are energetically allowed and the scattering is fully quantum mechanical. Even at a temperature of 1 mK, only a few partial waves in the scattering process are allowed, especially for the lighter alkalis as shown in the last column of Table 1.

Applications

Atomic Clocks and Tests of Local Position Invariance

The method proposed here provides an attractive alternative to direct laser cooling and optical state preparing of trapped ions for operation as an atomic clock. There are several advantages:

1) The optical transition in ions, used for cooling and optical pumping, is always in the ultra-violet. Indeed, Hg^+ , one of the most attractive clock atoms with a 40.5 GHz hyperfine clock transition, requires uv light at 194 nm, nearly into the vacuum ultraviolet spectral region. Although laser light at 194 nm has been generated via optical frequency doubling and additional nonlinear optical mixing, the process is costly since multiple visible lasers with watts of output power together with delicate doubling crystals are required. This procedure is to be contrasted with the relative ease which diode laser cooling of atoms in a MOT has become. Visible light from small solid state diode lasers (as used in CD players, for example) is carried by optical fibers and split into 3 intersecting retro-reflected circularly polarized beams[11]. This technology is at the center of today's optical industry insuring a ready supply of off-the-shelf components.

2) The clock transition in the Hg^+ ion is detected by the generation of Li^+ , a by-product of the spin dependent charge transfer to the laser cooled neutral. This is a natural synergy of cold collisions between heavy trapped ions and a light spin polarized neutral atom. An ion trap whose rf electric trapping field is set in frequency and amplitude to confine Hg^+ will eject the lightweight Li^+ since the amplitude of its driven motion is so much greater. This ejected Li^+ ion can be detected with nearly 100% efficiency with channeltron electron multipliers surrounding the trap. This novel detection process has enormous energy leverage since a 40.5 Ghz microwave photon (2×10^{-4} eV) absorbed in the Hg^+ ion will trigger the ejection of a 100 eV or more Li^+ ion, Signal to noise in the clock resonance, with 100% detection efficiency, would allow $10^{14} \sim 10^{15}$ short term stabilities which enter the 10^{17} stability regions with only a few hours averaging time.

3) The ions will be cooled to the temperature of the laser cooled neutrals, i.e., 1K for the LVIS/MOT earth based cold beam source and much lower for space based ultra-cold beams where gravitational deflection of a slow beam is much reduced. The second order Doppler shift of the clock transition in the ion is reduced to below 10^{-15} allowing clock stabilities into the 10^{17} region.

4) This technique is non-resonant, that is, without changing the light source/cold atom source, the trapped ion species could be changed and cooling, state selection, and resonance detection would be expected to precede as described above. The electron spin alignment between the colliding neutral and ion still mediates the close in collision dynamics and charge exchange even when the ion has more than one electron outside a closed shell, All diatomic molecules have binding and anti-binding states, determined by the relative orientation of the spins of the colliding partners[12]. Thus ions with large ground state splittings, even into the Thz regime, could readily be investigated with little change in experimental apparatus. This could not be easily done with

conventional uv optical pumping techniques

5) Multiple species of ions could be trapped simultaneously (eg., Hg^+ and Cd^+) and operated as two clocks in a single apparatus. This is important for certain clock comparison tests of the Equivalence Principle where Local Position Invariance demands that all atomic clocks run at the same rate independent of location. A coupling of the atomic fine structure constant, α , to the gravitational potential would force clocks of different atomic number Z to change in relative rate [13]. Two clocks in a single apparatus passing near the sun (where gravitational potentials are the largest in the solar system) could be compared to one another onboard a small spacecraft without sending a stable clock signal **downlink** from the spacecraft to be compared to an earthbased clock. This eliminates the need for an ultra-stable downlink, nearly impossible over a baseline near the sun. This self contained onboard null measurement also eliminates the need to determine the s/c trajectory to sub-millimeter accuracy as required in the separated clock comparison where one clock is on earth with the other in space.

Initial Laboratory Measurements

The initial experimental apparatus will consist of a MOT source of cold atoms in the configuration recently demonstrated by Lu et. al [7]. This low velocity intense source (LVIS) of cold atoms is a simple variation of a MOT trap and will produce a beam of density 10^9 to 10^{10} / cm^3 at speeds corresponding to 1K effective temperature. This beam will be passed down the axis of a linear ion trap containing a cloud of Hg^+ ions as shown in Figure 2.

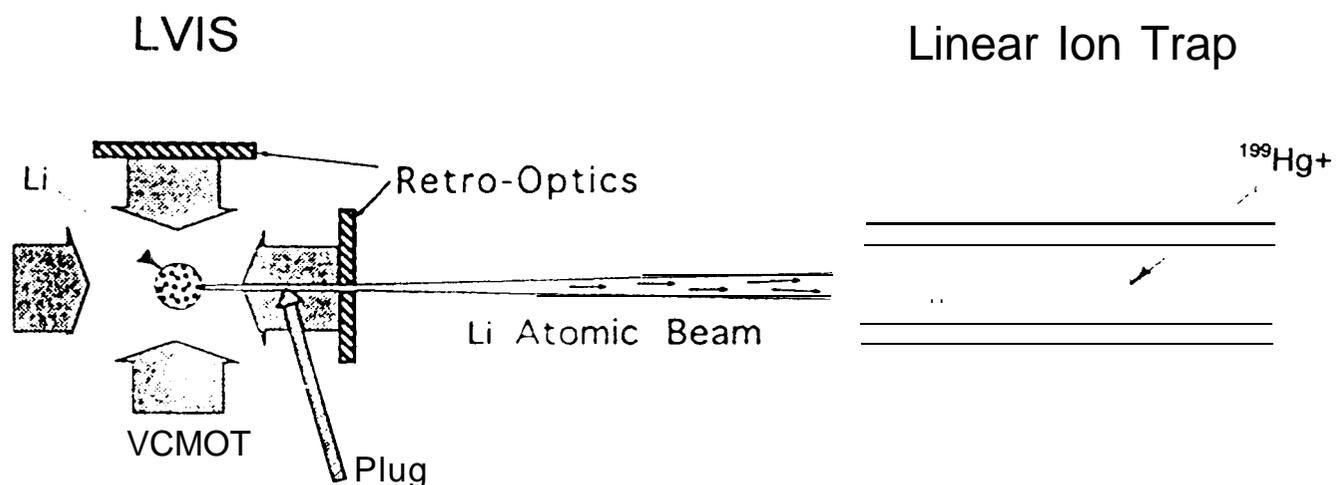


Figure 2: Schematic of the combination neutral and ion trap configuration, Neutral Lithium atoms exit a MOT in the LVIS configuration [7] and pass down the axis of a linear ion trap [16] containing $^{199}\text{Hg}^+$ ions.

The ion trap region will be surrounded by two or more channel electron multipliers to measure the Li^+ ion by-product of the charge exchange $\text{Hg}^+ + \text{Li} \rightarrow \text{Hg} + \text{Li}^+$. The lithium ion is ejected immediately after formation because of the mass selectivity of the quadrupole ion trap. In this configuration the charge transfer cross-section will be measured. Several linear ion traps have been used as the basis of a Hg^+ frequency standard [14]. Only the LVIS source with lasers will need to be built and mated to the ion trap vacuum system.

The LVIS beam can be optically pumped before entering the ion trap region and its polarization state optically monitored just **after** exiting the trap. In this way spin dependent charge exchange rates and spin exchange rates could be studied as shown in Figure 3. The experimental signature of the spin dependence of the charge transfer, i.e., that spin parallel reactions $\text{Hg}^+(\uparrow) + \text{Li}(\downarrow) \rightarrow \text{Hg} + \text{Li}^+$ precede much more **slowly** than the spin anti-parallel reaction $\text{Hg}^+(\downarrow) + \text{Li}(\uparrow) \rightarrow \text{Hg} + \text{Li}^+$ would be a flux of Li^+ ions from the trap following a microwave induced electron spin flip in the Hg^+ ion sample.

The spin exchange reactions would change the spin state of the transmitted alkali atom which could be optically monitored at the exit to the trap region. The ion cloud can also be optically pumped with a discharge lamp as done in the Hg^+ clock operation.

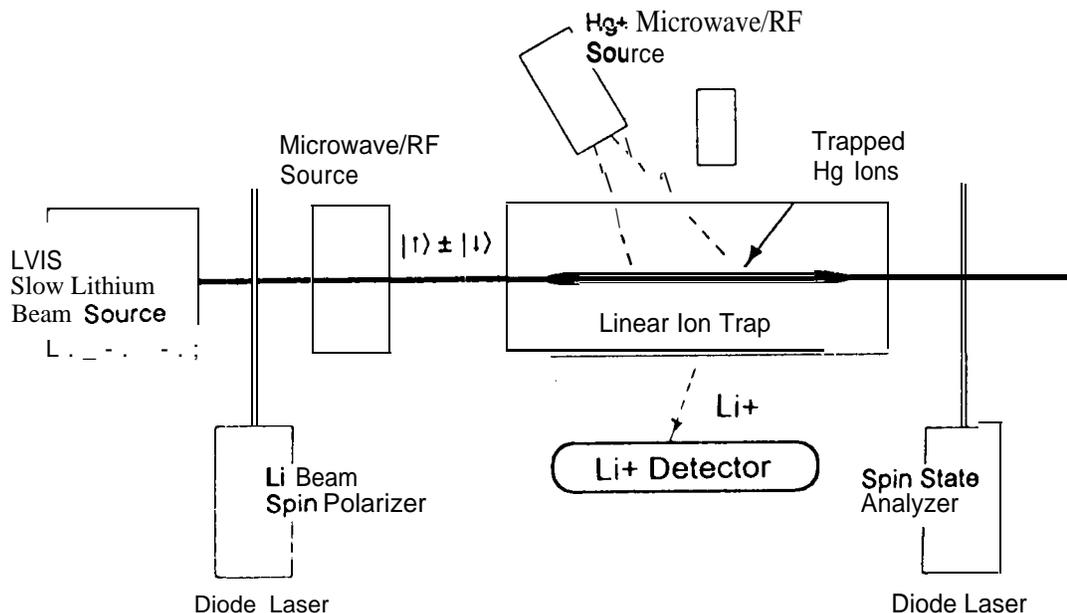


Figure 3: A low velocity intense source (LVIS) [7] generates a beam of cold lithium atoms which are spin polarized via optical pumping and pass down the axis of a linear ion trap containing Hg^+ ions. Charge transfer $\text{Hg}^+ + \text{Li} \rightarrow \text{Li}^+ + \text{Hg}$ is signalled by Li^+ ions ejected from the trap and collected in the surrounding channel electron multipliers. Spin exchange reactions with the Li or heavier slow alkali atom will result in a depolarization of the neutral beam and will be detected by optical fluorescence from the spin state analyzer as the spin states are re-aligned.

The proposed trapped ion atomic clock which uses cold atom spin exchange and **collisional** cooling seems well suited for the micro-gravity environment. The ion cloud is contained in a trap and is quite tolerant of departures from a perfect zero-g environment. The cold atoms are used to cool and monitor the ion internal state, a much less critical role than when the atoms serve as the reference for the actual clock. A high Q clock resonance in freely floating neutral atoms **will** demand a strictly low g environment. That is, **phase shifts** between successive Ramsey pulses due to a slight movement of the neutrals relative to the microwave source during the clock precession time, will make an apparent frequency **shift** of the clock transition. This is analogous to cavity end to end phase shifts in conventional beam tubes. Spin stabilization of the spacecraft, the cheapest means for s/c attitude control, will not be practical for such zero-g neutral atom clocks. Ions **confined** to an **rf trap** would operate quite well in such a spacecraft even with cold atoms as a source of state preparation and cooling since the ions are strictly confined relative to the microwave source.

References

- [1] P. S. Julienne and F. H. Mies, *J. Opt. Soc. Am. B* 6,2257 (1989). J. Wiener, *ibid*, 2270 (1989).
- [2] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, *Science* 269, 198 (1995).
- [3] R. L. Walsworth, E. M. Mattison, E. R. Orteiza, R. E. Stoner, K. Y. N. Tan, R. F. C. Vessot, and A. I. Yu, *Proc. 5th Symposium on Frequency Standards and Metrology*, 187 (1995).
- [4] H. G. Dehmelt, *Adv. At. Mol. Phys.*, 3,53 (1967), and 5, 109 (1969).
- [5] H. M. Gibbs and G. G. Churchill, *Phys. Rev. A* 3, 1617 (1971).
- [6] D. Rapp and W. E. Francis, *J. Chem. Phys.* 37,2631 (1962).
- [7] Z. T. Lu, K. L. Corwin, M. J. Renn, M. H. Anderson, E. A. Cornell, and C. E. Wieman, *Phys. Rev. Lett.* 77, 3331 (1996).
- [8] D. J. Larson, J. C. Berquist, J. J. Bollinger, W. M. Itano, and D. J. Wineland, *Phys. Rev. Lett.* 57, 70 (1986).
- [9] R. J. Knize, Z. Wu, and W. Happer, *Adv. At. Mol. Phys.* 24,223 (1988).
- [10] R. W. Molof, H. L. Schwartz, T. M. Miller, and B. Bederson, *Phys. Rev. A* 10, 1131 (1974).
- [11] E. L. Raab, M. Prentiss, A. Cable, S. Chu, and D. E. Pritchard, *Phys. Rev. Lett.* 59,2631 (1987).
- [12] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules*, 2nd Ed., 1989, Krieger Publishing Co., Malabar, Florida, USA.
- [13] J. D. Prestage, R. L. Tjoelker, and L. Maleki, *Phys. Rev. Lett.* 74,3511 (1995).
- [14] J. D. Prestage, R. L. Tjoelker, G. J. Dick, and L. Maleki, *J. Mod. Opt.* 39,221 (1992).