PRECISION MASS SPECTROMETRY OF IONS

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Overview

We compare the masses of single ions to 1 part in 10^{11}. This is an order of magnitude more accurately than our previous comparisons and firmly establishes our atomic mass measurements as the most accurate in the world. This dramatic improvement was achieved by implementing simultaneous cyclotron frequency comparisons of two ions in a Penning trap in order to eliminate the effect of magnetic field noise on the measured ratio of frequencies. We have measured four mass ratios to about 1 part in 10^{11} with diverse applications including a new and precise test of $E=mc^2$ by "weighing" γ-rays. In addition, we have discovered a novel cyclotron frequency shift arising from polarization forces that allows us to monitor the quantum state of a single molecular ion for days to weeks. From the size of the measured cyclotron frequency perturbations, we can determine the dipole moments of molecular ions— quantities not otherwise measureable.

In previous measurements made with single ions, we measured a total of 14 neutral masses with typical accuracies of 1 part in 10^{10}, ranging from the masses of the proton and neutron to the mass of ^{133}Cs [1-3] all with accuracies one to three orders of magnitude higher than the previously accepted values. Our mass measurements make important contributions in both fundamental physics and metrology, including:

- an 80-fold improvement of the current γ-ray wavelength standard by using $E = \Delta mc^2$ to determine the energies of ^{14}N neutron capture γ-rays (widely used as γ-ray calibration lines).

- opening the way for an atomic standard of mass by replacing the "artifact" kilogram mass standard with a crystal of pure silicon and our accurate determination of the atomic weight of ^{28}Si.

We achieved our previous accuracy of roughly 10^{-10} by measuring the cyclotron frequency of a *single* molecular or atomic ion in a Penning trap which consists of a highly uniform magnetic field combined with a much weaker electric field which provides confinement along the magnetic field lines. We measured a mass ratio by comparing the cyclotron frequencies $\omega_c = qB/mc$ of two ions alternately confined in the trap. We monitor an ion's axial oscillation by detecting the tiny currents (~10^{-14} A) induced in the trap electrodes. To measure such a small current requires an extremely sensitive detector, and we are fortunate to have improved the ultrasensitive superconducting electronics we developed for this application [4] by switching to an order of magnitude quieter DC SQUID.

We have developed a π-pulse method to coherently swap the phase and action of the cyclotron and axial modes [5]. Therefore, although we detect only the axial motion directly, we can

determine the cyclotron frequency by measuring the phase accumulated in the cyclotron motion in a known time interval. We can measure the phase of the cyclotron motion to about 10 degrees, yielding a precision of 10^{-10} in the cyclotron frequency for a one minute measurement. By measuring the frequencies of the other two normal modes of ion motion in a Penning trap, we can correct for electrostatic shifts in the cyclotron frequency to better than 10^{-12}.

We have also developed techniques for quickly isolating single ions in the trap by selectively driving the axial motion of the unwanted ions so that they neutralize on the trap electrodes. The entire ion-making process is fully computer controlled, and we can cycle from an empty trap to having a cooled single ion in about 3 minutes under optimal conditions.

Recent Progress

During the past year, we performed *simultaneous* cyclotron frequency comparisons of ions confined in the same Penning trap for the four pairs $^{33}S^+$ / $^{32}SH^+$, $^{29}Si^+$ / $^{28}SiH^+$, $^{13}C_2H_2^+$ / $^{14}N_2^+$, and $^{12}CO^+$ / $^{14}N_2^+$ all with relative accuracies $\leq 10^{-11}$. Our previous method of *alternately* measuring the cyclotron frequencies was limited almost entirely by temporal fluctuations of the magnetic field which are typically $3x10^{-10}$ (at night, much worse by day) during the several minutes required to trap a new single ion.

Our new simultaneous two ion technique has the advantages of a balance over a spring scale over the single ion technique. Importantly, it eliminates the effect of magnetic field variation on the cyclotron frequency ratio, yielding shot-to-shot noise in the ratio of ~ 7 x 10^{-11} after only three minutes of phase evolution. We have demonstrated precisions below $5x10^{-12}$ by averaging for periods of 12 hours.

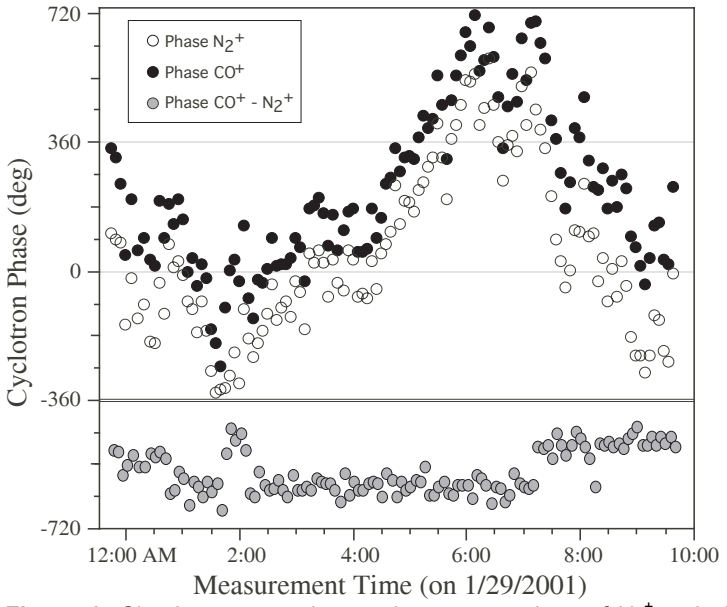

Figure 1 Simultaneous cyclotron phase comparison of N_2^+ and CO^+ after a phase evolution time of 240 seconds is shown in the upper graph. The lower graph demonstrates the excellent common mode rejection of the magnetic field noise when the measured phases are subtracted yielding a single shot precision of ~ 7 x 10^{-11} in the cyclotron frequency ratio. The sudden discrete jumps correspond to the CO^+ molecule changing its quantum rotational state by aborbing or emitting blackbody photons.

We have achieved averaging intervals lasting as long as 60 hours all under automated computer control and even during the daytime when magnetic field noise from the nearby subway prevents *alternate* ion comparisons with useful precision.

Simultaneously comparing the cyclotron frequencies of two ions of different species in the same trap offers the best protection against both magnetic field fluctuations and noise arising from the trapping voltage, but it does introduce new complications: ion-ion perturbations and systematic shifts due to spatial field inhomogeneities. In previous work studying the classical, two-body problem of two ions in a single Penning trap (both analytically [6] and with numerical models [7]), we found that the Coulomb interaction between the ions couples the nearly frequency-degenerate magnetron modes into a center of mass mode and a separation mode for which the ion-ion spacing is constant. In contrast, the several kHz difference in the cyclotron frequencies causes these modes to remain uncoupled. The ion-ion perturbation of the cyclotron frequency ratio is below 10^{-11} for separation distances >600μm.

The key to controlling systematics in this experiment lies in measuring and controlling the two magnetron modes, as these determine the location of the ions in the trap (center of mass mode) and relative to each other (separation mode). The center of mass mode can be observed and changed using small RF pulses to couple the ions' center of mass magnetron motion to the detected (and damped) axial mode. We then discovered a unique coupling technique that transfers angular momentum in either direction between the center of mass mode and the separation mode. The ion-ion separation is impossible to see directly, but is inferred from the modulation of the axial frequency when a small electrostatic anharmonicity is applied to observe the ions swap in and out of the trap center (see Fig 2). This swapping is due to the beating of the center of mass and separation magnetron modes, the latter shifted by the electric potential between the ions. It is a very accurate measure of the ion-ion separation.

Our ability to control the motion of the two ions is so complete that in the cases of $^{33}S^+$ / $^{32}SH^+$ and $^{29}Si^+$ / $^{28}SiH^+$, we performed a complete set of measurements at various separations using only *one ion each* of the rare isotopes $^{33}S^+$ and $^{29}Si^+$ over a week of measurements.

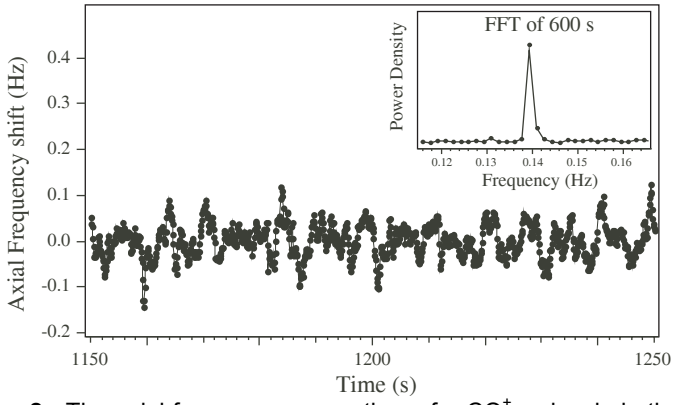

Figure 2. The axial frequency versus time of a CO^+ molecule in the same trap as an N_2^+ molecule. A small anharmonicity causes the axial frequency to depend on the radial position of the ion. The power spectrum (inset) reveals a single peak indicative of the beating of the magnetron separation and center of mass modes.

Using our control of the ion motions in our trap we have explored systematic errors due to both ion-ion interaction and trap imperfections. Figure 3 is an example of the observed variation of the measured cyclotron frequency ratio versus ion-ion separation. While the separation is changed by only a factor of ~2, we expect the systematic errors to change by ~30 over this range due to the high power scaling with ion-ion separation of even the lowest systematic errors. New and careful measurements of the trap magnetic field inhomogeneities and electrostatic anharmonicities combine with knowledge of the trap scaling to predict that the error on the measured ratio is less than 10^{-11} for separations between 600 and 900 μm.

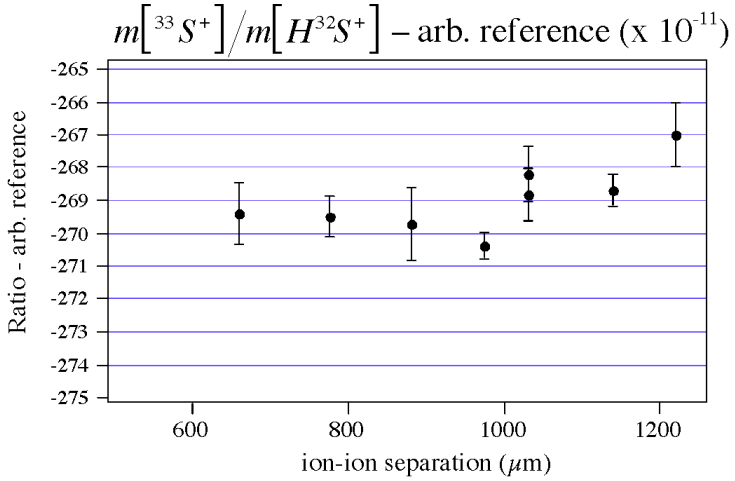

Figure 3 Cyclotron Frequency Ratio vs Ion-Ion Separation. Each division corresponds to a change in the ratio of 1 part in 10^{11}. The observed variation at large separations arises from uncertainties in our knowledge of the trap anharmonicities.

Subthermal Measurements

Using a DC SQUID (with a technical noise floor 10 times smaller than the RF SQUID it replaced) has allowed us to measure the 4K noise currents in our high-Q coupling circuit and employ negative feedback to reduce the noise currents to an effective temperature as low as 0.5K (see Figure 4) [8]. The feedback also reduces the observed ion current, but the coupling circuit's back-action on the ion, which causes the motion to damp, is reduced allowing the ion signal to be averaged for longer before the thermal noise in the detector circuit rethermalizes it. Using this technique, we have observed factors of ~ 2, 2 and 4 improvement in determining the ion's phase, amplitude and axial frequency respectively. This electronic refrigeration should also yield subthermal ion motion since the coupling circuit acts as the reservoir for cooling the ion between measurements.

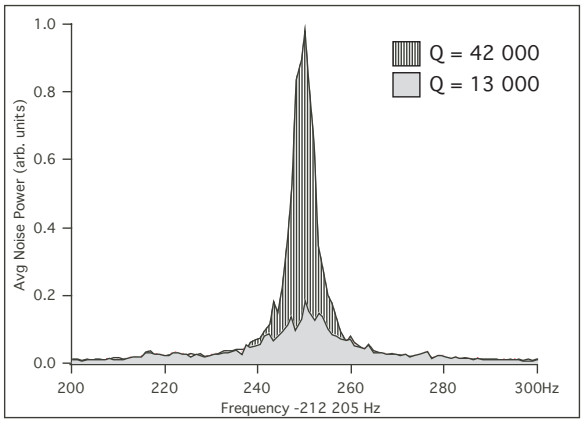

Figure 4 Thermal profile of the high-Q superconducting detection circuit before (Q = 42 000) and after (Q = 13 000) feedback. The effective temperature is proportional to the integrated power. Here a factor of 3 reduction is observed and we have achieved a reduction of ~8.

For simultaneous cyclotron frequency measurements, the leading source of random error are the frequency shifts associated with thermal variations in the cyclotron radius. The frequency shifts arise from special relativity, magnetic field inhomogeneities, and ion-ion interactions at the smallest separations. Combining the technique of squeezing that we previously demonstrated [9] and proposed [10] with this electronic refrigeration should reduce the shot-to-shot fluctuations of the cyclotron frequency ratio to a few times 10^{-12}

for all but the lightest species. We feel further justified in exploring such techniques because they are of general interest to the precision measurement community.

Observing the Quantum State of a Single Molecule with Polarization Forces

As shown in Figure 1, the measured cyclotron frequency ratio of CO^+/N_2^+ exhibits sudden discrete jumps as large as 1 part in 10^9. Correcting for external field variations with an improved external field monitor revealed that it is actually the CO^+ ion whose cyclotron frequency is changing at these jumps. The CO^+ ion is a highly polarizable molecule and the motional electric field which it sees in its rest frame due to its motion along its cyclotron orbit is several 100V/cm. The induced dipole effectively shifts the center of charge relative to the center of mass, altering the cyclotron frequency. Because both the sign and magnitude of the polarizability change with the quantum state of the molecule, the cyclotron frequency shift changes when the ion absorbs or emits a black-body photon, which happens every few hours at our 4 Kelvin termperature. We can actually discriminate three distinct cyclotron frequency values corresponding to the (J=0, M=0), (J=1, M=±1) and (J=1, M=0) lowest rotational states of the molecule. From the size of the shifts we will extract the dipole moment for CO^+, the first dipole moment measured for any charged molecule.

Testing $E=mc^2$ by weighing γ-rays

The relationship $E=mc^2$ will be tested by comparing our measured mass differences between $^{29}Si^+$ / $^{28}SiH^+$ and $^{33}S^+$ / $^{32}SH^+$ to the energy of the emitted γ-rays in the neutron capture processes converting ^{28}Si to ^{29}Si and ^{32}Si to ^{33}Si, i.e.

$$\frac{\Delta M}{10^3 N_A h} c_m^2 = \frac{c_{em}}{\lambda_S} - \frac{c_{em}}{\lambda_D}$$. put h/lambda on the right, use 1 c-value

We expect that the ultimate sensitivity of this comparison will be limited by the accuracy of the γ-ray wavelength measurements performed by NIST to 1 part in 10^7. This test of special relativity does not depend on measuring spatial anisotropy as do the Michelson-Morley and Hughs-Drever experiments. As a result, this test does not require the assumption that the Cosmic Microwave Background is the preferred frame in order to set limits on various parameters quantifying the violation of special relativity.

A violation of mass-energy equivalence can be thought to signify two different fundamental velocities in the theory of special relativity: an electromagnetic speed of light c_{em} which is the speed with which light propagates in a vacuum and a distinct mechanical speed of light c_m which is the limiting velocity of a massive particle. Labeling which speed of light is referred to, the comparison can be expressed in terms of accurately measured quantities as

$$\frac{\Delta M}{10^3 N_A h} c_m^2 = \frac{c_{em}}{\lambda_S} - \frac{c_{em}}{\lambda_D} \quad .$$

The mass difference ΔM in u comes from our measured mass ratios at 10^{-11} and the measured mass ratio H_2 / D known to a similar absolute accuracy as our measurements. The deuteron binding energy is included as determined from the wavelength λ_D of the emitted γ-rays in its own neutron capture process. These two corrections allow for the fact that we do not directly measure the neutron mass. Lastly, the Planck's constant h (used to convert frequency to energy) and the Avogadro's number N_A (used to convert ΔM from u to kg), are combined to form the Molar-Planck constant which is known to better than 10^{-8} from measurements of the fine structure constant as discussed in the next section. Turning things around, improved measurements of the

wavelengths λ_S , λ_D and the assumption $c_{em} = c_m$ would allow a competitive determination of the Molar-Planck and fine structure constants.

Mass Measurements: fine structure α and molar Planck N_Ah constants

Previous to our most recent mass comparisons, we measured the atomic masses of ^{133}Cs, ^{85,87}Rb, and ^{23}Na with accuracies of better than 0.2 ppb [3, 11]. This is at least a 100-fold improvement in accuracy for these species. ^{133}Cs and ^{87,85}Rb are the heaviest atoms we have yet measured and extend our measured mass range by a factor of more than 3. We also demonstrated our ability to make accurate measurements with multiply-charged ions, e.g. Cs^{3+}. Our ability to make sub-ppb measurements of masses from 133 to 1 amu and our use of various charge states to do so have demonstrated the remarkable flexibility of our apparatus.

Our measurements of ^{133}Cs, ^{85,87}Rb, and ^{23}Na will make significant contributions to fundamental physics and metrology including:

- new determinations of the molar Planck constant, N_Ah, with precision ~10 ppb;
- new determinations of the fine structure constant, α, with precision ~5 ppb;
- providing reference masses for mass measurements of radioactive nuclei - which are important for testing models of astrophysical heavy element formation.

Our sub-ppb measurement of the mass of Cs will provide a direct measurement of N_Ah to an accuracy near 10^{-8}. The following expression shows how this is achieved by combining our mass of Cs with measurements of the recoil velocity of a Cs atom, after absorbing a photon of a precisely measured wavelength:

$$\lambda v = \frac{h}{m} = \frac{10^3 N_A h}{M}.$$

This equation follows directly from the simple quantum relationship between de Broglie wavelength and momentum. N_Ah is of great importance metrologically since N_A links SI mass units to atomic mass units. The most accurate determination of N_A is currently provided by combining N_Ah with the recent 87 ppb measurement of Planck's constant h performed at NIST. Possible future measurements of the photon recoil in Rb and Na BEC's, in combination with our measurements of their masses, will allow even more accurate determinations of N_Ah, possibly at the few ppb level of accuracy.

A new value of the fine structure constant will be extracted from the above determination of N_Ah using:

$$\alpha^2 = \frac{2R_\infty}{c}\frac{1}{M_p}\frac{M_p}{M_e}\left(N_A h\right).$$

The Rydberg constant R_∞ has been measured to an accuracy of 0.008ppb, M_p/M_e is known to 2 ppb, and we have determined the atomic mass of the proton M_p to 0.5 ppb (Van Dyck's group at UW has a preliminary result for M_p at 0.14ppb). Thus a measurement of N_Ah at the 2 ppb level can determine α to about 1 ppb. This new fine structure constant value will be the second most precise measurement of α and will serve as a stringent test of QED's ability to predict the electron's g-2. In addition, its conceptual simplicity is especially important in view of the recent 55 ppb adjustment of the fine structure constant value extracted from g-2.

Future Plans

Our method for making *simultaneous* cyclotron frequency comparisons has eliminated the effects of magnetic field fluctuations, bringing us within reach of our long term goal of attaning an accuracy of a few parts in 10^{-12}. Improving accuracy to this level should be achieved by making a double trap wherein the two ions are contained in neighboring wells, measured simultaneously, and swapped between them to eliminate systematic errors. This level of accuracy will allow further contributions to fundamental physics:

- Measurement of the ^{3}H - ^{3}He mass difference, which is important in ongoing experiments to determine the electron neutrino rest mass.
- Determination of excitation and binding energies of atomic and molecular ions by weighing the associated small decrease in mass, $\Delta m = E_{bind} / c^2$ (we must reach our ultimate goal of a few parts $\times 10^{-12}$ to make this a generally useful technique).
- Improvement of traditional applications of mass spectrometry resulting from our orders of magnitude improvement in both accuracy and sensitivity.

Recent Publications

Rainville, S., J.K. Thompson, D.E. Pritchard, “Single-ion mass spectrometry at 100 ppt and beyond.” *Can. J. Phys.* **80**(11) 1329 (2002).

Rainville, S.*, et al.*, “Precise Measurements of the Masses of Cs, Rb and Na - A New Route to the Fine Structure Constant.” *Hyperfine Interactions*, **132**: 177 (2001)

Bradley, M.P., J.V. Porto, S. Rainville, J.K. Thompson, and D.E. Pritchard, “Penning Trap Measurements of the Masses of ^{133}Cs, $^{87,85}Rb$, and ^{23}Na with Uncertainties $\leq$0.2 ppb.” *Phys. Rev. Lett.* 83: 4510 (1999).

Bradley, M.P., *A Sub-ppb Measurment of the Mass of Cesium for a New Determination of the Fine-Structure Constant*, Ph.D. Thesis, Physics Department, MIT, 2000.

Nguyen, R.N.V., *Loss Mechanisms in Superconducting Niobium Coils*, B.Sc. Thesis, Physics Department, MIT, 1998.

Bradley, M., F. Palmer, D. Garrison, L. Ilich, S. Rusinkiewicz and D.E. Pritchard, “Accurate mass spectrometry of trapped ions”, *Hyperfine Interactions* 108: 227-238 (1997).

DiFilippo, F., V. Natarajan, M. Bradley, F. Palmer, and D.E. Pritchard, “Accurate atomic mass measurements from Penning trap mass comparisons of individual ions,” *Physica Scripta* T59: 144-54 (1995).

Natarajan, V., F. DiFilippo, and D. E. Pritchard, “Squeezed states of classical motion in a Penning trap,” *Phys. Rev. Lett.* 74: 2855 (1995).

References

1. Natarajan, V.*, et al.*, *Precision Penning Trap Comparison of Nondoublets - Atomic Masses of H, D, and the Neutron.* Physical Review Letters, 1993. **71**(13): p. 1998-2001.

2. Difilippo, F.*, et al.*, *Accurate Atomic Masses for Fundamental Metrology.* Physical Review Letters, 1994. **73**(11): p. 1481-1484.

3. Bradley, M.P.*, et al.*, *Penning trap measurements of the masses of Cs-133, Rb-87,Rb- 85, and Na-23 with uncertainties <= 0.2 ppb.* Physical Review Letters, 1999. **83**(22): p. 4510-4513.

4. Weisskoff, R.M.*, et al.*, *Rf Squid Detector for Single-Ion Trapping Experiments.* Journal of Applied Physics, 1988. **63**(9): p. 4599-4604.

5. Cornell, E.A.*, et al.*, *Mode-Coupling in a Penning Trap - Pi-Pulses and a Classical Avoided Crossing.* Physical Review A, 1990. **41**(1): p. 312-315.

6. Cornell, E.A.*, et al.*, *2 Ions in a Penning Trap - Implications for Precision Mass-Spectroscopy.* Physical Review A, 1992. **45**(5): p. 3049-3059.

7. Rusinkiewicz, S., *Simultaneous Two Ion Mass Spectroscopy*. 1995, Massachusetts Institute of Technology.

8. Pritchard, D.E. and J.K. Thompson. *Mass Spectrometry at 100 parts per trillion*. in *Les Houches Summer School - Trapped Particles and Fundamental Physics*. 2000. Les Houches, France.

9. Natarajan, V., F. Difilippo, and D.E. Pritchard, *Classical Squeezing of an Oscillator for Subthermal Noise Operation.* Physical Review Letters, 1995. **74**(15): p. 2855-2858.

10. Difilippo, F.*, et al.*, *Classical Amplitude Squeezing for Precision-Measurements.* Physical Review Letters, 1992. **68**(19): p. 2859-2862.

11. Rainville, S.*, et al.*, *Precise Measurements of the Masses of Cs, Rb and Na - A New Route to the Fine Structure Constant.* Hyperfine Interactions, 2001. **132**: p. 177.