Precision Mass Spectrometry of Ions

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Introduction

We compare the masses of single ions with accuracies typically 10^{-10} — firmly establishing our atomic mass measurements as the most accurate in the world. To date we have measured a total of 14 neutral masses, 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 ÒartifactÓ kilogram mass standard with a crystal of pure silicon and our accurate determination of the atomic weight of ^{28}Si.

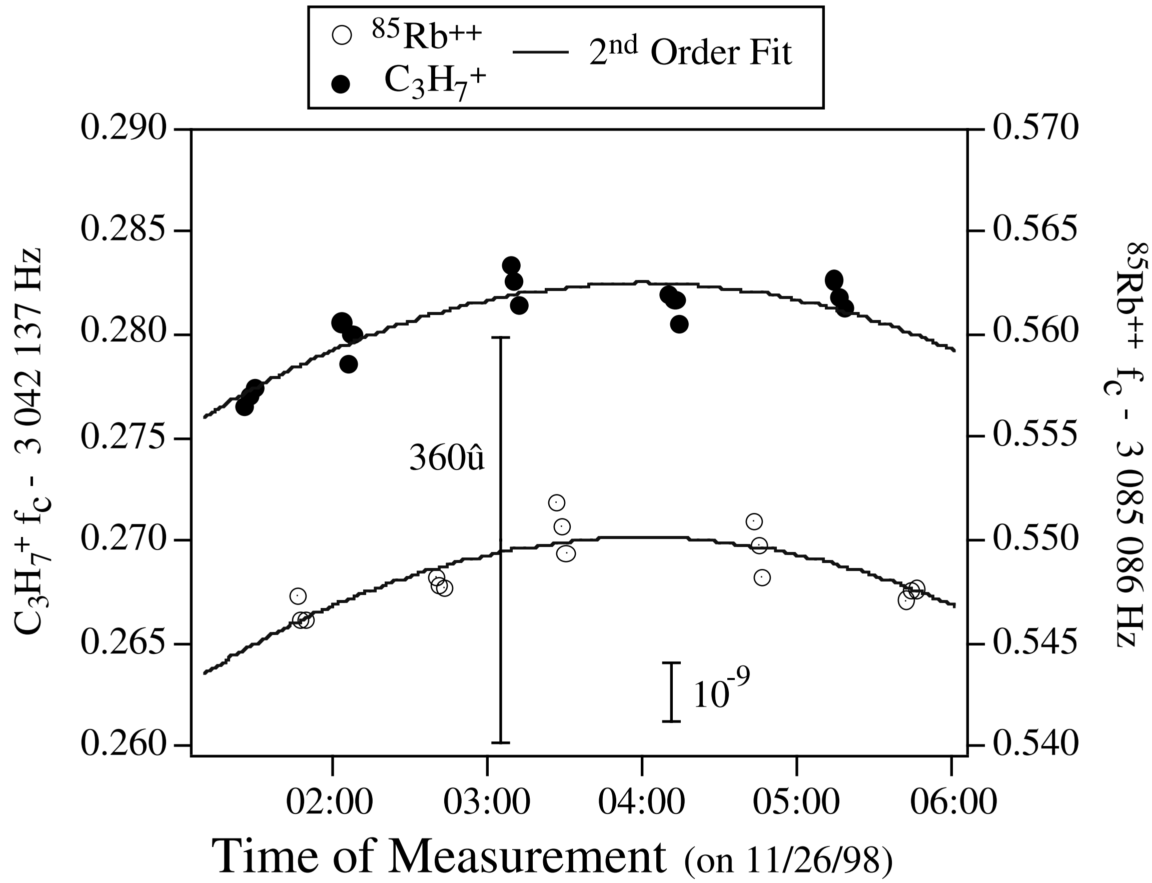

Figure 1 Cyclotron frequency as a function of time for alternate $C_3H_7^+$ and $^{85}Rb^{++}$ ions in our Penning trap. The frequencies are obtained after a 50s integration of cyclotron phase. The solid line is a polynomial fit to the drift in the field common to both ions.

We achieve our current 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 measure a mass ratio by comparing the cyclotron frequencies $\omega_c = q\,B/m\,c$ of two ions alternately confined in the trap (see Fig. 1). 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 a 10x quieter DC SQUID.

We 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 much better than 10^{-10}.

We have also developed techniques for quickly isolating single ions in the trap by selectively driving the axial motion of the unwanted ions. 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

1. Electronic Refrigeration of Detector and Ion

During the past year, we have developed a technique which uses feedback to reduce the effective temperature of the superconducting transformer used to detect the ion's axial motion below the ambient 4K. This electronic refrigeration is possible because the quiet dc SQUID allows us to accurately measure the 4K Johnson noise in the transformer and to add negative feedback to reduce the noise (see Fig. 2).

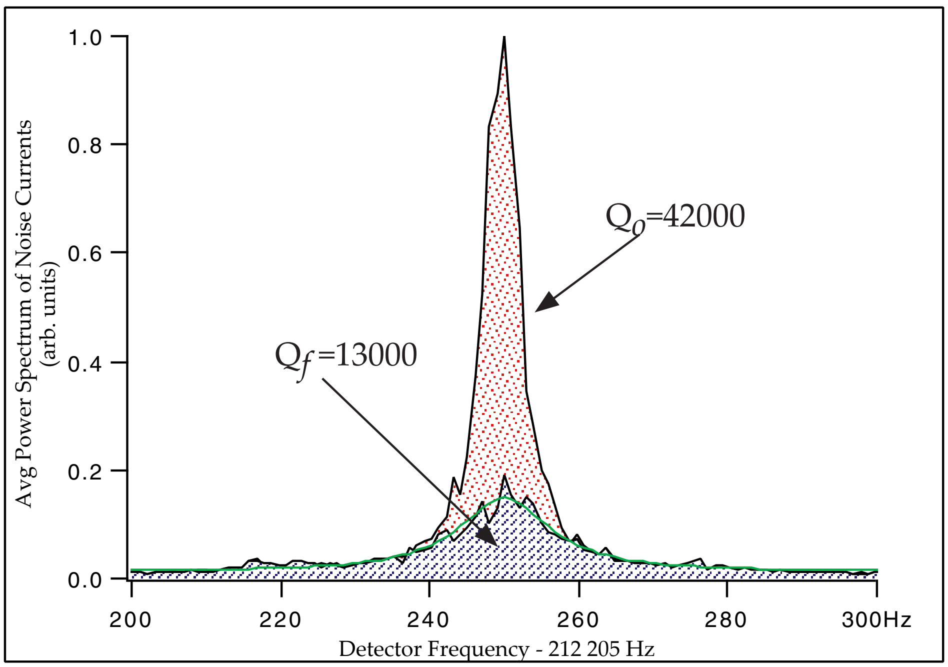

Figure 2 Electronic Refrigeration of Noise Currents. The average power spectrum of the detected Johnson noise current in the superconducting resonant transformer with and without negative feedback. In this example, both the Q and effective electronic tempertature (which is just proportional to the area under the curves) are reduced by a factor of 3. In addition to improved signal to noise, this also results in a colder ion because the ion comes to thermodynamic equilibrium with the subthermal noise currents.

The negative feedback reduces the transformer voltage across the trap which is responsible for damping the ion's axial motion. The S/N is improved because the ion damps more slowly thus allowing a longer signal averaging time. Restating this, even though the ratio of instantaneous ion current to Johnson noise current remains unchanged by the feedback, the ion's signal is made more monochromatic and can be detected with higher S/N against the broadband Johnson noise background. The increased S/N has improved our ability to measure the ion's axial frequency, phase, and amplitude by factors of ≈ 4, 2, and 2 respectively.

A further benefit of this electronic refrigeration is that the ion comes to thermodynamic equilibrium with the subthermal transformer resulting in a colder ion. Achieving subthermal ion temperatures is crucial for future plans to improve the accuracy of our mass measurements because present thermal variation of the cyclotron orbit size coupled with special relativity and magnetic field inhomogeneities results in shot-to-shot cyclotron frequency noise at several parts in 10^{11} for m/q ~20 and close to a part in 10^{10} for lighter species such as ^{3}He and ^{3}H. The present ratio of dc SQUID noise to the transformer's Johnson noise currently sets a rough upper limit of reducing the transformer's effective temperature by a factor of 9 and thus the shot-to-shot relativistic cyclotron frequency noise by 3.

In addition, we have proposed several methods of classical squeezing with parametric drives to reduce amplitude fluctuations [6], and demonstrated the simplest of these [7], reducing the effects of thermal noise by about a factor of two. Combining electronic refrigeration and classical squeezing will open the door to a dramatic improvement in the resolution of mass spectrometry once the effects of magnetic field fluctuations are reduced.

2. Mass Measurements: fine structure α and molar Planck $N_A h$ constants

Most recently, we measureed the atomic masses of ^{133}Cs, ^{85,87}Rb, and ^{23}Na with accuracies of better than 0.2 ppb [3]. 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, $N_A h$, 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 $N_A h$ 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. $N_A h$ 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 $N_A h$ with the recent 87 ppb measurement of PlanckÕsconstant h performed at NIST. Possible future measurements of the photon recoil in Rb and Na BECÕs, ri combination with our measurements of their masses, will allow even more accurate determinations of $N_A h$, possibly at the few ppb level of accuracy.

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

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

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 DyckÕs group at UW has a preliminary result for M_p at 0.14ppb). Thus a measurement of $N_A h$ at the 2 ppb level can determine _ 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 QEDÕs abilityto predict the electronÕs g-2. In addition, its conceptual simplicity is especially important in viewof the recent 55 ppb adjustment of the fine structure constant value extracted from g-2.

3. Future Plans

Fluctuations in our magnetic field (see Fig. 1) limit our current accuracy to at best 5×10^{-11}. Our long term goal is to reach an accuracy of a few parts in 10^{-12}, an improvement by more than one additional order of magnitude. Improved accuracy will allow further contributions to fundamental physics:

¥ Measurement of the ^3H - ^3He mass difference, which is important in ongoing experiments to determine the electron neutrino rest mass.

¥ Checking the relationship $E = mc^2$ to a part in 10^7 by weighing γ-rays from neutron capture by ^{32}S whose wavelength is being measured by a NIST group; this will also provide an independent determination of $N_A h$ and the fine structure constant.

¥ 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 in 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.

The effect of magnetic field fluctuations will be greatly reduced by measuring the cyclotron frequencies of two ions trapped in the same field at the same time [8]. We have already demonstrated the capability of two ion measurements to reduce the effects of field fluctuations. We have also developed theoretical understanding of the dynamics of two simultaneously trapped ions and built hardware that will allow us to control the relative motion of the ions. This is important to minimize the systematic errors introduced by ion-ion interactions.

We have also studied a second method for overcoming the limits due to magnetic field fluctuations: placing two ions in closely adjacent traps, and swapping them between the two traps. This will make our measurements insensitive to fluctuations in the magnetic field which are common to both traps; however, relative time variations of the magnetic field between the two traps will remain as a source of noise. To combat this source of noise, we have designed a general system of coils which will suppress time variations of the first order magnetic field gradient by up to two orders of magnitude. This has just been written up for publication. Even without this, using one of the traps as a ÒholdingtankÓfor the ion of a pair which is not being measured could increase the rate of measurements by a factor of four while simultaneously decreasing the time for field fluctuations, decreasing our statistical uncertainty by a factor of 2. This double trap technique has the advantage of not introducing complex ion-ion perturbations, and theoretical estimates predict systematic errors below a few parts in 10^{12} for this scheme..

Recent Publications

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

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8. 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.