PRECISION MASS SPECTROMETRY OF IONS

Sponsors

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Academic and Research Staff:

Prof. David E. Pritchard

Graduate Students

Simon Rainville

James K. Thompson

Undergraduate Students

Nisha Nath

Overview

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 "artifact" kilogram mass standard with a crystal of pure silicon and our accurate determination of the atomic weight of ^{28}Si.

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 $\omega_c = qB/mc$ 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.

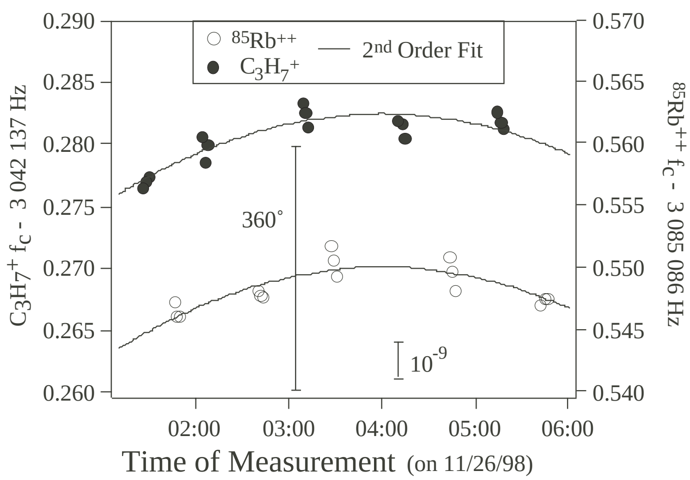

Figure 1 Cyclotron frequency as a function of time for alternate $C_3H_7^+$ and $^{85}Rb^{++}$ ions in our Penning trap. The frequencies are obtained after a 50s integration of cyclotron phase. The solid line is a polynomial fit to the drift in the magnetic field common to both ions.

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

During the past year, we demonstrated *simultaneous* cyclotron frequency comparisons using N_2^+ and CO^+ simultaneously confined in the same trap (see Fig. 2) . Our previous method of *alternately* measuring the cyclotron frequencies was limited almost entirely by temporal fluctuations of the magnetic field which are typically $3x10^{-10}$ during the several minutes required to trap a new single ion. This new technique 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. Repeated simultaneous cyclotron frequency comparisons have

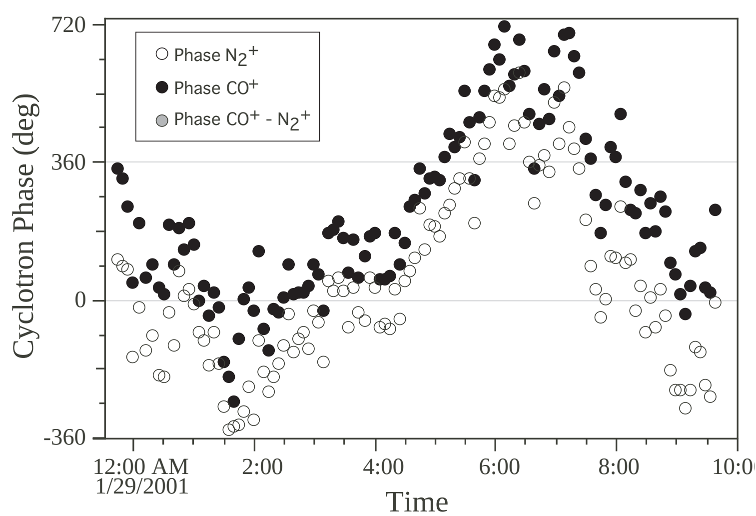

Figure 2 Simultaneous cyclotron phase comparison of N_2^+ and CO^+ after a phase evolution time of 240 seconds. The common drift of the cyclotron phases demonstrates the excellent common mode rejection of magnetic field noise. In a single shot, the cyclotron frequency ratio can be determined to ~ 7 x 10^{-11}. We are currently exploring ocassional and abrupt changes in the ratio which persist on time scales of hours.

been made for periods as long as 60 hours all under automated computer control and even during the daytime when magnetic field noise from the nearby subway would prevent *alternate* comparisons with useful precision.

Simultaneously comparing the cyclotron frequencies of two ions of different species in the same trap offers the best possible protection against magnetic field fluctuations but introduces 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 stretch mode for which the ion-ion spacing is constant. In contrast, the several kHz difference in the cyclotron frequencies causes ion-ion perturbation of the cyclotron frequency ratio to remain below 10^{-11} for separation distances of ~1mm.

Unfortunately, we have observed occasional abrupt changes in the measured cyclotron frequency ratio. We will attempt to understand these changes using a recently developed technique to monitor the radial magnetron motion of the ions as a function of time. This is done by introducing a small electrostatic anharmonicity and then monitoring the axial frequency shift resulting from changes in the radial position of the ion. We have observed modulation of the axial frequency at the expected frequency for beating of the center of mass and stretch magnetron modes against one another (see Fig 3). This frequency also serves as a very sensitive measure of the ion-ion separation distance which will be important for exploring the systematic shifts of the cyclotron frequency ratio as a function of radial separation.

We have also studied a second method for overcoming the limits due to magnetic field fluctuations which could be implemented: 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 been written up for publication. Even without this, using one of the traps as a "holding tank" for the ion of a pair which is not being measured could increase the rate of measurements by a factor of four decreasing our statistical uncertainty by a factor of 2 while simultaneously decreasing the time for field fluctuations. 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.

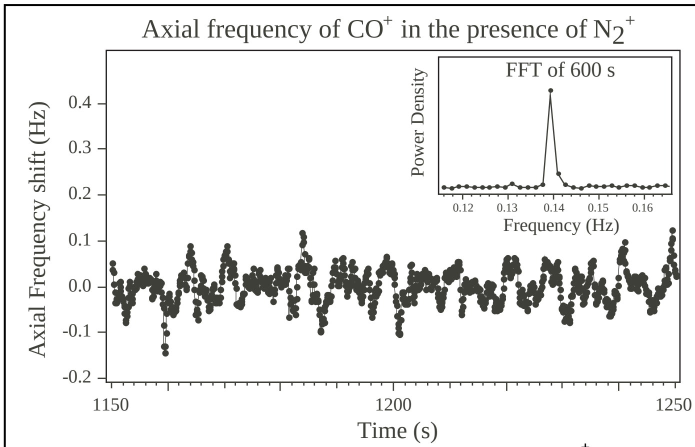

Figure 3. The axial frequency versus time of a CO^+ molecule in the same trap as an N_2^+ molecule. A small anharmonicity causes the axial frequency to depend on the radial position of the ion. The power spectrum (inset) reveals a single peak indicative of the beating of the magnetron center of mass and separation modes.

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

Most recently, we measured the atomic masses of ^{133}Cs, ^{85,87}Rb, and ^{23}Na with accuracies of better than 0.2 ppb [3, 8]. 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 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 $N_A h$, 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:

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

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 $N_A h$ 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[9].

Future Plans

Our method for making *simultaneous* cyclotron frequency comparisons has eliminated the effects of magnetic field fluctuations bringing us much closer to our long term goal of attaning 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 ^{3}H - ^{3}He 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 X 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., *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 ≤0.2 ppb." *Phys. Rev. Lett.* 83: 4510 (1999).

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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).

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