Overview

We can now compare the masses of single ions with relative accuracy below 1 part in $10^{11}$. This is an order of magnitude more precise than our previous comparisons, and an advance in the state-of-the-art by nearly 4 orders of magnitude since we started this experiment in 1983. It 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. This elegant and novel technique has allowed us to:

- demonstrate an unprecedented level of control of the motion of two different ions in a Penning trap;
- measure four mass ratios to about 1 part in $10^{11}$ with diverse applications
- discover a novel cyclotron frequency shift arising from polarization forces that allows us to monitor the quantum state of a single molecular ion nondestructively.
- perform a test of $E=mc^2$ at 3 parts in $10^7$, an improvement by a factor of 40 over previous tests
- determine the dipole moment of a molecular ion more accurately than in previous work.

In previous measurements made with single ions, we obtained a total of 14 neutral atomic 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, all with accuracies one to three orders of magnitude higher than the previously accepted values [1, 2]. Our atomic mass measurements made important contributions in both fundamental physics and metrology, including:

- an 80-fold improvement of the $\gamma$-ray wavelength standard by using $E = \Delta mc^2$ to determine the energies of $^{14}$N neutron capture $\gamma$-rays (widely used as $\gamma$-ray calibration lines);
- opened 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. A Penning trap consists of a highly uniform magnetic field, which provides radial confinement, combined with a much weaker electric field that confines ions harmonically along the magnetic field lines. We measured a mass ratio by comparing the cyclotron frequencies $\omega = q B / m c$ of two ions alternately confined in the trap, with preferably one of them rich in the atomic mass standard, $^{12}$C. We monitor an ion’s axial
oscillation by detecting the tiny currents (~10^{-14} A) induced in the trap electrodes. Measuring 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 [3] by switching to an order of magnitude quieter DC SQUID. 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.

We have developed a π-pulse method to coherently swap the phase and action of the cyclotron and axial modes. 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 ratio to better than 10^{-12}.

Recent Progress

Over the past two years, we have developed novel techniques to perform simultaneous cyclotron frequency comparisons of ions confined in the same Penning trap. We compared the four pairs \(^{33}\text{S}^{+} / {^{32}\text{S}}^{+}, \text{Si}^{+} / {^{28}\text{Si}}^{+}, \text{^{13}C}_2\text{H}_2^{+} / {^{14}\text{N}_2}^{+}, \text{and} \text{^{12}CO}^{+} / {^{14}\text{N}_2}^{+}\) 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 3\(\times\)10^{-10} (at night, much worse by day) during the several minutes required to trap a new single ion.

With respect to the single ion technique, our new simultaneous two-ion technique has the same advantages that a mass balance has with respect to a spring scale. Importantly, it eliminates the effect of magnetic field variation on the cyclotron frequency ratio, yielding shot-to-shot noise in the ratio of \(\sim 7\times 10^{-11}\) after only three minutes of phase evolution. We have demonstrated precisions below 5\(\times\)10^{-12} by averaging for periods of 12 hours. Furthermore, the two-ion technique allows us to perform mass measurements even during the daytime when magnetic field noise from the nearby subway prevents *alternate* ion comparisons with useful precision. We have achieved averaging intervals lasting as long as 60 hours - all under automated computer control.
Simultaneously comparing the cyclotron frequencies of two ions different species in the same trap offers the best protection against errors from fluctuations in the trapping voltage as well as magnetic field fluctuations, but it does introduce new complications: ion-ion perturbations and systematic shifts due to spatial magnetic field inhomogeneities. This technique rests on our studies of the classical, two-body problem of two ions in a single Penning trap (both analytically [4] and with numerical models [5]). 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 [4]. In contrast, the several kHz difference in the cyclotron frequencies causes these modes to remain uncoupled and only slightly perturbed (the ratio of cyclotron frequencies is typically perturbed by less than $10^{-11}$ for separation distances greater than 600 µm). Over the last few years, we have experimentally verified these predictions, and we have exploited the dynamics of the coupled ions in the trap to control their relative position and study the systematic errors in our mass comparisons.

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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 [6]. 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. The measured swapping frequency then serves as a very accurate measure of the ion-ion separation.

![Figure 1](image-url) Simultaneous cyclotron phase comparison of $\text{N}_2^+$ and $\text{CO}^+$ 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 $\sim 7 \times 10^{-11}$ in the cyclotron frequency ratio. The sudden discrete jumps occur whenever the $\text{CO}^+$ ion changes its quantum rotational state by absorbing or emitting a blackbody photon.
Our ability to control the motion of the two ions is so complete that in the cases of $^{33}\text{S}^+$ / $^{32}\text{SH}^+$ and $^{29}\text{Si}^+$ / $^{28}\text{SiH}^+$, we performed a complete set of measurements at various separations using only one ion each of the rare isotopes $^{33}\text{S}^+$ and $^{29}\text{Si}^+$ over several weeks of measurements. Our excellent ion control has allowed us to explore the two significant sources of new systematic errors in this technique: ion-ion interaction and trap imperfections [7]. The largest potential source of systematic error arising from ion-ion interactions results from a possible asymmetry in the cyclotron radii of the two ions.

The magnitude of this shift has been experimentally confirmed by purposely making the two cyclotron radii differ by 20%, and observing the predicted change in the difference between the cyclotron frequencies (to within $1 \times 10^{-11}$). During our precise mass comparisons, we obviously make the cyclotron radii equal to each other to within 2%. At a separation of 750 µm, this uncertainty translates into an upper limit of $4 \times 10^{-12}$ for the potential systematic error on the mass ratio due to ion-ion interaction. This uncertainty decreases very rapidly as the separation distance, $\rho_s$, is increased (at least as $\rho_s^{-5}$) and is represented by the hatched band on the left of the two plots in Fig. 3.

Careful measurements of the trap magnetic field inhomogeneities and electrostatic anharmonicities, combined with our precise knowledge of the ion-ion separation, have enabled us to optimize the trap to make the measured cyclotron frequency difference nearly independent of trap field imperfections [8]. Uncertainties in our measurements of the trapping fields and of the ion-ion separation (~5%) translate into an upper limit of $4 \times 10^{-12}$ for the possible uncanceled systematic error at a separation of 750 µm. This uncertainty grows very rapidly as the separation distance, $\rho_s$, is increased (at least as $\rho_s^{-5}$) and is represented by the gray band on the right of the two plots in Fig. 3.

![Axial frequency of CO⁺ in the presence of N₂⁺](image)

**Figure 2** The axial frequency versus time of a CO⁺ molecule in the same trap as an N₂⁺ 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.

![Figure 3 Cyclotron Frequency Ratio vs Ion-Ion Separation for two data sets.](image)

**Figure 3** Cyclotron Frequency Ratio vs Ion-Ion Separation for two data sets. Each division corresponds to a change in the ratio of 1 part in $10^{11}$. The bands represent the upper limits on the systematic errors from...
ion-ion interactions (hatched area) and trap field imperfections (gray area). The solid line shows our best estimate of each mass ratio, with a 1σ confidence interval indicated by the dashed lines.

The observed variation in the measured cyclotron frequency ratio versus ion-ion separation for two data sets is shown in Fig. 3, with superimposed bands of predicted upper limits on systematic errors from ion-ion interaction and trap imperfections. The separation is changed by a factor of ~2, implying that the systematic errors change by ~30 over this range due to the high power scaling with ion-ion separation of even the lowest systematic errors. The data provides strong evidence that the systematic errors have been overestimated, because the measured ratio varies with ion-ion separation by much less than predicted from our estimates (the bands). Nevertheless, we conservatively relied on the above estimates to obtain the final error on the four ratios that we measured with the two-ion technique (see Table 1), and claim only the rms error of the central points as the error, rather than the standard deviation of the mean.

As discussed below, the two-ion technique lead to the discovery of the effect of polarization forces on precise cyclotron frequency measurements. Since all of our measurements involved polarizable species (except M[14N2]/M[13C2H2]), our measured frequency ratios had to be corrected for this effect before unperturbed ratios could be reported. Using available molecular spectroscopic data, the fractional cyclotron frequency shifts of the N=0 ground state for 28SiH+ and 32SH+ were estimated to be (–7.4 ± 1.5) × 10⁻¹² and (–47± 14) × 10⁻¹². In the case of M[CO]/ M[14N2], the rotational state dependence of the CO+ polarizability could be directly observed in our data, allowing us to determine both the unperturbed ratio and the molecular dipole moment of CO+. Although this is the most accurate determination of the dipole moment of any charged molecule, its uncertainty dominates the final error on our reported M[CO]/ M[14N2] (and similarly for the sulfur ratios). However, ab initio calculations of electric dipole moments and of the polarizabilities of the first few rotational states for these simple molecules can be carried out with greater accuracy, which would sharpen the determination of the mass ratio from our data.

Our silicon ratio measurement leads directly to a new value for the atomic mass of 29Si with a relative precision of 7 × 10⁻¹¹ (limited by the current uncertainty on the mass of 28Si), an order of magnitude improvement over the current most precise value [9]:

\[ M[^{29}\text{Si}] = 28.976 494 662 5(20) \text{ u} \]

### Table 1

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Measured value</th>
<th>Factor of improvement in uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>M[14N2] / M[13C2H2]</td>
<td>0.999 421 460 888 (7)</td>
<td>12</td>
</tr>
<tr>
<td>M[CO]/ M[14N2]</td>
<td>0.999 598 887 617 (15)</td>
<td>3</td>
</tr>
<tr>
<td>M[33S]/ M[32SH]</td>
<td>0.999 744 164 347 (16)</td>
<td>394</td>
</tr>
<tr>
<td>M[29Si]/ M[28SiH]</td>
<td>0.999 715 124 181 (7)</td>
<td>114</td>
</tr>
</tbody>
</table>

### Testing E=mc² by weighing γ-rays

Einstein’s famous relationship \( E=mc^2 \) has been tested by comparing our measured mass differences between \( ^{29}\text{Si}^+ / ^{28}\text{SiH}^+ \) and \( ^{33}\text{S}^+ / ^{32}\text{SH}^+ \) to the energy of the emitted γ-rays in the neutron capture processes converting \(^{28}\text{Si}^+ \) to \(^{29}\text{Si}^+ \) and \(^{32}\text{Si}^+ \) to \(^{33}\text{Si}^+ \), i.e.
\[ \Delta m \: c^2 = E_{\lambda} = \frac{hc}{\lambda}. \]

This test of special relativity does not depend on measuring spatial anisotropy as do the Michelson-Morley and Hughes-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

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

The mass difference \( \Delta M \) (in relative atomic mass units, u) comes from our measured mass ratios at \( 10^{-11} \) and the measured mass ratio \( m[H_2]/m[D] \), which is known to a similar absolute (but not relative) accuracy as our measurements. The deuteron binding energy is included as determined from the wavelength \( \lambda_D \) of the emitted \( \gamma \)-rays in its own neutron capture process [10]. 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 \( \Delta M \) 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. Combining the values of \( \lambda_D, \lambda_S \) and \( \lambda_{ai} \) with the our measured ratios from Table 1 lead to two independent tests of the relationship \( E=mc^2 \) shown in Fig. 4. Combined together, these results give

\[ 1 - \left( \frac{c_{em}}{c_m} \right) = (-1.3 \pm 1.6) \times 10^{-7}. \]

Even though experimental tests of other assumptions of special relativity can derive much more stringent limits on potential violations, the above condition is the most precise direct test of \( E=mc^2 \), by a factor of about 40. Turning things around, improved measurements of the wavelengths \( \lambda_S, \lambda_D \) and the assumption \( c_{em} = c_m \) could allow a competitive determination of the Molar-Planck and fine structure constants.
Observing the Quantum State of a Single Molecule with Polarization Forces

As shown in Fig. 1, the measured cyclotron frequency ratio of CO\(^+\)/N\(_2\)\(^+\) exhibited 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 that it sees in its rest frame due to its motion along its cyclotron orbit is several 100 V/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 blackbody photon, which happens every few hours at our 4 Kelvin temperature. In our data, 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 extracted a 2 % value for the dipole moment for CO\(^+\):

\[ \mu = 1.025(15) \text{ e}a_0, \]

which is in agreement with the calculated value (\(e\) is the charge of the electron and \(a_0\) is the Bohr radius). This is one of the few experimental measurements of the dipole moment of a charged molecule.

Mass Measurements: fine structure \(\alpha\) and molar Planck \(N_A h\) constants

Prior to developing the two-ion technique, we measured the atomic masses of \(^{133}\text{Cs}\), \(^{85,87}\text{Rb}\), and \(^{23}\text{Na}\) with accuracies of better than 0.2 ppb. This is at least a 100-fold improvement in accuracy for these species. The atoms \(^{133}\text{Cs}\) and \(^{87,85}\text{Rb}\) are the heaviest masses we have yet measured and extend our measured mass range by a factor of more than 3. It 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.

The measurements of \(^{133}\text{Cs}\), \(^{85,87}\text{Rb}\), and \(^{23}\text{Na}\) made significant contributions to fundamental physics and metrology including:

- new determinations of the molar Planck constant, \(N_A h\), with precision \(\leq 15\) ppb;
- new determinations of the fine structure constant, \(\alpha\) with precision \(\leq 8\) 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 \(10^5\). 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. A preliminary value for \(h/m\) was recently reported with an uncertainty of 15 ppb\(^3\). \(N_A h\) 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:
\[ \alpha^2 = \frac{2R_\infty}{c} \frac{1}{M_e} (N_A h). \]

Thus a measurement of \( N_A h \) at the 2 ppb level can determine \( \alpha \) to about 1 ppb. The Rydberg constant, \( R_\infty \), has been measured to an accuracy of 0.007 ppb, and the atomic mass of the electron, \( M_e \), is known to 0.4 ppb. At 7 ppb, this new fine structure constant value is be the second most precise measurement of \( \alpha \) and serves 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 attaining an accuracy of a few parts in \( 10^{-12} \). Further studies of systematic errors might reveal that this technique already allows this level of precision. Improving accuracy to this level could also be achieved in the future by making a double trap wherein the two ions are contained in neighboring wells, measured simultaneously, and swapped between them to eliminate systematic errors. In either case, the current and improved levels of accuracy will allow further contributions to fundamental physics including:

- Measurement of the \( ^3\text{H} - ^3\text{He} \) 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, \( \Delta m = E_{\text{bind}} / c^2 \) (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**


References

Chapter 14: Precision Mass Spectrometry of Ions