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Mass ratio of two ions in a Penning trap by alternating between the trap center and a large cyclotron orbit

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Abstract

We have implemented a technique for precision mass comparison of two ions trapped simultaneously in a Penning trap in which each ion is alternately positioned at the center of the trap – where the cyclotron frequency is measured – and in a large cyclotron "parking" orbit. Systematic shifts in the cyclotron frequency ratio have been studied by comparing ${}^{13}C_2H_2{}^+/{}^{14}N_2{}^+$ and ${}^{14}N_2{}^+/{}^{28}Si^+$. Using the method to compare ${}^{28}SiH_3{}^+/{}^{31}P^+$ we have obtained a new atomic mass for ${}^{31}P$, M[^{31}P] = 30.973 761 999 7 (61) u.

Keywords: Atomic mass; Precision measurement; Penning trap

1. Introduction

The highest precision atomic mass comparisons to date have been measurements of the mass ratios ${}^{12}C^{16}O^+/N_2{}^+$, ${}^{13}C_2H_2{}^+/N_2{}^+$, ${}^{28}SiH^+/{}^{29}Si^+$ and ${}^{32}SH^+/{}^{33}S^+$, all at sub-10^{-11} fractional precision [1–3]. These were carried out by *simultaneously* comparing the cyclotron frequencies of the two (single) ions in a cryogenic Penning trap: the ions, separated by about 1 mm, orbited the center of the trap symmetrically, 180° apart, in a coupled magnetron mode. The simultaneous measurement essentially eliminated the main contributions to the statistical uncertainty in high-precision mass comparisons, namely the effects of time variation in the magnetic field and difficulties in precisely measuring the ions' axial frequencies. However, this method requires that the individual ions' magnetron frequencies be nearly degenerate and hence that the ions be of very similar mass. It also relies on sophisticated techniques for the manipulation and monitoring of the coupled magnetron motion, and a careful characterization of the trapping fields [4,5].

Short of simultaneous cyclotron frequency measurement, to reduce the effects of magnetic field variation, it is necessary to interchange between the ions as quickly as possible. (A complementary approach is to engineer a highly stable superconducting magnet, as has been implemented by Van Dyck et al. [6,7].) One way to achieve this is to develop efficient ways of creating and isolating single ions in the Penning trap [8–10]. Another way, as was first demonstrated in a 10^{-10} mass comparison of the anti-proton and the H^- ion to test the CPT theorem [11,12], is to trap both ions simultaneously, but to position one ion at the center of the trap, where its cyclotron frequency is measured, while the second is "parked" in a large radius (∼1 mm) cyclotron orbit. The ions are then interchanged to measure the second ion's cyclotron frequency, and so on. As with the simultaneous two-ion technique, a single pair of ions can be trapped for several days, enabling precise measurements on ions that are difficult to make or are rare. Parking in a cyclotron orbit rather than a magnetron orbit is more convenient since the cyclotron frequencies of even close "mass-doublets" are well separated, in contrast to the magnetron frequencies, so that the motions remain uncoupled. This allows a simple interchange procedure. Although this method has been used for mass-1 ions in Refs. [11,12], it has not, to our knowledge, been applied to heavier ions where the effects of ion–ion coulomb interaction on the measured cyclotron frequencies are larger.

Our aims were to implement and test the method using the previously known ratios ${}^{13}C_2H_2{}^+/{}^{14}N_2{}^+$ and ${}^{14}N_2{}^+/{}^{28}Si^+$, and to then apply the method to obtain a new atomic mass for ${}^{31}P$ from the comparison ${}^{28}SiH_3{}^+/{}^{31}P^+$. The two latter ratios involve ions that are minority fractions of electron ionisation of the parent gases SiH_4, PH_3. These would be difficult and tedious to mea-

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sure accurately using the techniques described in [8–10], which we ourselves have used for mass measurements of ^{32}S, $^{84,86}Kr$, and $^{129,132}Xe$ [13]. As it happened, we found quasi-systematic shifts to the resulting mass ratios, possibly unrelated to the two-ion technique, at the level of $\sim 1 \times 10^{-10}$. In the time available we have not resolved this systematic and so have been unable to fully exploit the improved statistical precision the method allows. Our measurement of the mass of ^{31}P at $<2 \times 10^{-10}$ provides an addition to the table of "precisely known masses" that can be used as references for other mass measurements. We also had a specific motivation in that we are interested in studying cyclotron frequency shifts due to polarizability [2] in the molecular ion PH^+. This has a $^2\Pi_{1/2}$ electronic structure with Λ-type doubling, and hence a relatively large polarizability. The independent measurement of the mass of ^{31}P obtained here is useful for interpreting the measurements on PH^+ that will be published elsewhere.

This paper is organized as follows. We first describe our implementation of the technique and give a brief discussion of expected systematic effects due to the presence of the outer ion. We then summarize our results for $^{13}C_2H_2{}^+/^{14}N_2{}^+$ and $^{14}N_2{}^+/^{28}Si^+$, which we treat as tests; and then of the ratio $^{28}SiH_3{}^+/^{31}P^+$, which leads to a new mass measurement of ^{31}P.

2. Implementation of the technique

The measurements were carried out using the precision single-ion Penning trap mass spectrometer originally developed at MIT [14,15] but now relocated to Florida State University. An important component of this apparatus is an efficient computer control system designed for work with two ions [4,5]. Mass comparisons at the 10^{-10} level using the relocated apparatus, and the original method of making and measuring on each ion alternately have been described in detail in Ref. [13], so only some details are given here.

The Penning trap, with hyperbolic electrodes with characteristic size $d = 5.5$ mm [16], is mounted in a cryogenic vacuum jacket in the bore of a 8.5 T superconducting magnet with typical field stability of $\sim 10^{-9}$/h. The leading electrostatic field imperfection, "C_4", is compensated by guard-ring electrodes between the end-caps and ring electrodes. All radial rf drives, and radial–axial coupling rf drives, are applied to one half of one of these guard-rings. Damping and detection of the ion's axial motion – the only signal we extract, and always near $f_z = 213{,}400$ Hz – is obtained by adjusting the trap voltage to bring it to resonance with a $Q = 33{,}000$ superconducting coil connected across the end-caps. The coil is inductively coupled to a dc-SQUID. For mass-28 ions the axial damping time constant for an ion on resonance with the coil is about 1 s.

Our procedure starts by making the first ion in our usual way. We inject a small burst of gas along the trap axis in coincidence with a $\sim$5 nA electron beam from a field-emission point below the trap. The desired ion is axially cooled by bringing it to resonance with the coil. All other ions are eliminated by axially exciting them and then "dipping" – i.e., lowering the ion cloud towards the lower end-cap so the unwanted ions strike it and are lost. The cyclotron and magnetron motions of the single desired ion are cooled by coupling them to the damped axial mode using drives at the respective coupling frequencies $f_{cc} = f_{ct} - f_z$, and $f_{mc} = f_m + f_z$, where f_{ct} is the trap (or "modified") cyclotron frequency and f_m is the magnetron frequency. The first ion is then excited into a large cyclotron parking orbit, of radius up to 2 mm, by using a rf pulse of variable length close to the ion's trap cyclotron frequency. (For sufficiently short pulses and small detuning the cyclotron radius is proportional to the product of pulse amplitude and duration; we use a drive calibration derived from measurements of relativistic shifts using multiply charged ions.) The second ion is then made in the trap center, and other ions removed as before—but care is taken to axially cool both ions, by appropriately setting the trap voltage, before applying the dip. (Allowance is made for the 5–10 Hz shift in f_z of the outer ion due to the trap's electrostatic and magnetic imperfections, primarily B_2 ($-7.9\ (4) \times 10^{-8}$ mm^{-2}), and C_6 ($1.1\ (1) \times 10^{-3}$), coupled with the large cyclotron radius.) Once the two ions are made and other ions removed they can be interchanged as follows: first the outer ion's cyclotron radius is reduced to $\sim$50% by applying the cyclotron–axial coupling for typically 45 s. The inner ion is then excited to the large cyclotron orbit using a single cyclotron drive pulse. The formerly outer ion is then cooled all the way to the trap center by again applying cyclotron–axial coupling for 2–5 min. The resulting axial excitation is continuously monitored to ensure complete cooling. Both ions' magnetron motions are then cooled by applying the magnetron coupling drives at the respective frequencies for 15–30 s.

We saw no evidence of ion loss due to collisions in the swapping procedure. The cyclotron orbits of the two ions apparently cross with sufficient axial separation that they do not significantly interact. The ion lifetime was apparently limited by collisions with background gas molecules: the average lifetime of the ions in our trap increased with time since they were made; we would observe the loss of one ion, and the appearance (detected from perturbations to the remaining ion) of an ion of a different species. One $N_2{}^+/Si^+$ pair survived more than 7 days before the $N_2{}^+$ was lost, having crossed more than 250 times.

To check that the ions were excited to the same parking radius, a short cyclotron–axial coupling pulse was applied to the outer ion, and the resulting axial amplitude and frequency, both of which depend on the parking radius, were recorded. Any magnetron motion acquired by the outer ion was monitored by applying a magnetron–axial pi-pulse, after this ion had been cyclotron cooled, and recording the axial amplitude.

The cyclotron frequency of the inner ion was measured using the "PNP" technique [8,13,17]. After cyclotron and magnetron cooling the ion is excited into a $\sim$150 μm radius cyclotron orbit. The phase is then allowed to evolve, without any drive or damping, for a well defined "phase evolution time". The final phase of the cyclotron motion, φ_{ct}, is then read out by applying a pi-pulse at the cyclotron–axial coupling frequency, coherent with the cyclotron excitation pulse, resulting in axial excitation. The axial excitation is detected by the dc-SQUID as it is damped by the coil. The signal is then digitized and analysed to extract a phase, frequency and amplitude. The trap cyclotron frequency is hence obtained by varying the phase evolution time, t_{evol}, and obtaining f_{ct} as the slope $\Delta\varphi_{ct}/\Delta t_{evol}$. This is mainly defined by the longest and shortest t_{evol}'s. However, in order to determine the total number of 2π's to be added – requiring successively improved estimates of the cyclotron frequency – it is necessary to perform PNP's with intermediate t_{evol}'s. In our procedure we used a PNP sequence with 10 different t_{evols} from 0.2 to 58 or 74 s. The axial frequencies from the 10 PNP's are averaged to give a value of f_z to be associated with the f_{ct} from the 10 PNP sequence. The values for f_{ct} and f_z are then combined to produce a single value of the "free-space" cyclotron frequency f_c, using the "invariance theorem" [16]:

$$f_c^2 = f_{ct}^2 + f_z^2 + f_m^2, \tag{1}$$

where

$$f_m = (f_z^2/2f_{ct})[1 + (9/4)\sin^2\theta_{mag}]. \tag{2}$$

here θ_{mag} parameterizes the effects of trap tilt and ellipticity [16], and is obtained by a measurement of the magnetron frequency of each ion using the avoided crossing technique [17] at the start of each run. Because of the hierarchy of frequencies – for mass-28, $f_{ct} \cong 4.7$ MHz, $f_z \cong 213$ kHz, $f_m \cong 4.8$ kHz – a 10^{-10} measurement of f_c requires that f_{ct} be measured to the same precision while f_z be measured to better than 5×10^{-8}. With the above values of the trap magnetic and electrostatic field imperfections, the finite cyclotron radius and resulting axial amplitude do lead to shifts in the cyclotron frequency of order 10^{-9} for a single ion at the trap center. However, by working with mass-doublets, with fractional mass differences of 10^{-3} or less, these shifts are expected to be common to $\sim10^{-11}$ and so cancel in the ratio, as discussed in Ref. [13].

A typical run consists of a series of measurements of f_c obtained alternately for each ion. Depending on the cyclotron radius used for the outer ion, the ion swapping procedure takes 3–6 min, and the PNP sequence, with cyclotron cooling and magnetron cooling after each PNP, takes approximately 8 min. A single run can last up to 15 h before a liquid nitrogen jacket must be refilled.

The cyclotron frequency measurements obtained in a typical run for the ratio $^{13}C_2H_2^+/N_2^+$ are shown in Fig. 1. The point-to-point fluctuations in our measurements of f_c have a fractional standard deviation $\leq 3\times10^{-10}$ with contributions from short term variation in the magnetic field, and from the uncertainty in the measurement of the cyclotron phase and axial frequency from the single-ion axial ring-down signals, due to 4.2 K thermal noise in our detection circuit. The longer-term variation in f_c seen in Fig. 1 is caused by variation in the magnetic field, mainly due to causes internal to the superconducting magnet and its cryostat. (We use a flux-gate magnetometer to monitor ambient field variation in our laboratory and can correct our f_c measurements accordingly, but usually this does not result in a significant reduction in their variation.) Rather than simply averaging f_c for each ion over a run, we obtain improved statistical precision for the mass ratio by removing some of the common variance due to longer-term magnetic field drift. We do this by making a simultaneous least-squares fit of a single polynomial to both ions' f_c, but with an offset term between the ions proportional to the mass difference. (One ion's f_c would be pre-scaled using an initial estimate of the mass ratio if the ions are not close mass-doublets.) The optimum polynomial order is chosen from the variation of χ^2 using the F-test [14]. The statistical error (for a single run) is obtained from the fitting routine using standard least-squares methods. If the data is well described by a low-order polynomial, we find that the variation in the mass ratio obtained using different polynomial order fits is small compared to this statistical error.

Compared to remaking each ion every interchange this technique has potential for greatly improved precision because the interchange is faster, particularly if the ions are difficult to make and isolate, and the process is fully automatic, allowing much longer total data acquisition times. More care can also be taken to ensure the absence of other ions in the trap.

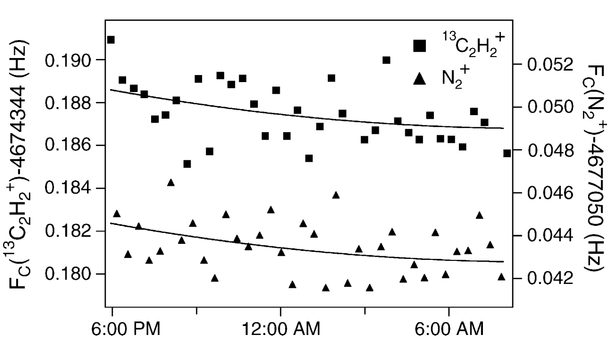

Fig. 1. Data for one run of cyclotron frequency measurements of a single $^{13}C_2H_2^+$ and $^{14}N_2^+$ pair trapped simultaneously in the Penning trap. The ions are alternated between the trap center and a large cyclotron parking orbit. In this case the simultaneous polynomial fit gives the ratio to a precision of 6.3×10^{-11}.

3. Shifts to the cyclotron frequency of the inner ion due to the outer ion

In this section we consider in an intuitive way the perturbations we expect to affect our measurement of the cyclotron frequency obtained from the PNP technique and Eq. (1). We first consider "static" effects where we simply average over the zeroth-order unperturbed motions of the two ions. We then discuss dynamical effects that take account of the motions.

3.1. Ring of charge model

To lowest order in the ion–ion coulomb interaction, because the relevant frequency differences are large compared to the inverse of the measurement times, we can approximate the effect of the parked ion (k) in the large cyclotron orbit on the inner ion (i) as that of a ring of charge q_k of radius ρ_{ck}. If the electrostatic potential near the trap center is expanded using the usual Legendre polynomial series [16]:

$$\varphi(\underline{r}) = (V_0/2)\sum_{l=2,4,\ldots} C_l (r/d)^l P_l(\cos\theta) \tag{3}$$

where d is the characteristic trap size parameter and V_0 is the voltage between the ring and end-caps, the perturbations to the coefficients C_l produced by the outer ion are given by [19]:

$$\Delta C_l(\rho_{ck}) = [2\Omega_z/\omega_z]P_l(0)(d/\rho_{ck})^{l-2}, \quad (4)$$

where $\Omega_z = \Omega_E^2/\omega_z$, $\Omega_E^2 = q_i q_k/[4\pi\varepsilon_0 m_i \rho_{ck}^3]$, and $\omega_z = 2\pi f_z$ (Ω_E^2, Ω_z are analogous to a spring constant and a "Rabi frequency", respectively, see Refs. [4,5,18]). These perturbations to the trap field coefficients can then be substituted into expressions for the anharmonic shifts to ion-i's eigen-frequencies due to finite amplitudes ρ_{ci}, a_{zi}, and ρ_{mi} [4,5,16]. (With d as the expansion parameter in Eqs. (3) and (4) the ΔC_l do not converge. Nevertheless the corresponding frequency perturbations do converge provided ρ_{ci}, a_{zi}, ρ_{mi} are small compared to ρ_{ck}.)

In our implementation of the PNP technique the trap cyclotron frequency f_{ct} is measured (during the phase evolution period) with relatively small axial and magnetron rms amplitudes of 35 and 8 μm, respectively, determined by the ion cooling procedure, but with a cyclotron radius ρ_{ci} of 140–160 μm. The axial frequency f_z is measured from the axial ring-down following the cyclotron-to-axial pi-pulse: the cyclotron and magnetron radii are small, but the initial amplitude of the axial motion $a_{zi}^{max} = \rho_{ci}(f_{ct}/f_z)^{1/2} \cong 750$ μm. Hence the dominant fractional shift to f_{ct} is due to finite ρ_{ci} and is given by

$$\Delta f_{ct}/f_{ct} \cong (f_z/f_{ct})^2(\Omega_z/\omega_z)[1/2 + 9/16(\rho_{ci}/\rho_{ck})^2 + 75/128(\rho_{ci}/\rho_{ck})^4 + 1225/2048(\rho_{ci}/\rho_{ck})^6 \ldots], \quad (5)$$

while that to f_z is due to finite a_{zi}, and at the start of the ring down, is given by

$$\Delta f_z/f_z \cong (\Omega_z/\omega_z)[-1/2 + 9/16(a_{zi}^{max}/\rho_{ck})^2 - 75/128(a_{zi}^{max}/\rho_{ck})^4 + 1225/2048(a_{zi}^{max}/\rho_{ck})^6 \ldots], \quad (6)$$

where the successive terms correspond to the contributions from C_2, C_4, C_6, C_8, etc.

The first terms in Eqs. (5) and (6), due to C_2, are independent of the inner ion's amplitudes. In our trap for mass-28, with ρ_{ck} = 1.2 mm, they result in substantial fractional shifts of $+1.7 \times 10^{-9}$ and -8.0×10^{-7} in f_{ct} and f_z, respectively. But a change in C_2 is equivalent to a change in trap voltage, so they cancel when substituted into Eq. (1) and produce no change to the measured "free space" cyclotron frequency f_c. For ρ_{ck} = 1.2 mm, $\Delta C_4 = 2.5 \times 10^{-5}$, a small value that can be nulled by a small adjustment of the guard-ring voltage, and $\Delta C_6 = -4.4 \times 10^{-4}$, which is smaller than, and in fact partly compensates our trap's inherent C_6. The shift to $\Delta f_{ct}/f_{ct}$ from these higher-order terms is $<10^{-10}$ and negligible here. The higher-order terms lead to a shift in $\Delta f_z/f_z$ at the start of the ring down ~+0.33 ($\Omega_z/2\omega_z$) corresponding to an (uncompensated) $+5.6 \times 10^{-10}$ shift in f_c. However, this represents an upper limit since the measurement of f_z is obtained from an average as the amplitude rings down. These shifts fall with increasing radius of the outer ion as $(\rho_{ck})^{-5}$ or faster. Moreover, by ensuring similar ρ_{ck} as the ions are interchanged, these shifts should cancel in the cyclotron frequency ratio.

This "ring of charge" model can be extended to include the effects of finite axial and finite magnetron motion for the outer ion a_{zk}, ρ_{mk} by correctly averaging over the respective motions. The results can be expressed in terms of Eq. (4) by writing:

$$\Delta C_l(\rho_{ck}, a_{zk}) = \Delta C_l(\rho_{ck})A_l(a_{zk}/\rho_{ck}), \quad (7)$$

$$\Delta C_l(\rho_{ck}, \rho_{mk}) = \Delta C_l(\rho_{ck})M_l(\rho_{mk}/\rho_{ck}). \quad (8)$$

Graphs of A_l and M_l are shown in Fig. 2. They show that finite axial motion of the outer ion reduces frequency shifts to the inner ion, while finite magnetron motion leads to an increase.

3.2. Frequency shifts due to the motion of the outer ion

The outer ion's cyclotron motion applies a rotating dipole drive to the inner ion leading to a non-resonantly driven amplitude:

$$\rho_{ci} = \Omega_E^2\rho_{ck}/[(\omega_{ctk} - \omega_{cti})(\omega_{ctk} - \omega_{mi})]. \quad (9)$$

For the "mass-doublets" we consider, the cyclotron frequency difference, $(\omega_{ctk} - \omega_{cti})/2\pi \geq 2700$ Hz, and this amplitude is <0.01 μm and negligible. As discussed in Refs. [4,5,18], the (non-resonant) cyclotron motion that ion-i induces on ion-k resonantly back-acts on ion-i and hence produces a second-order frequency shift:

$$\Delta\omega_{cti}^{(2)} \cong -\Omega_c^2/[4(\omega_{ctk} - \omega_{cti})], \quad (10)$$

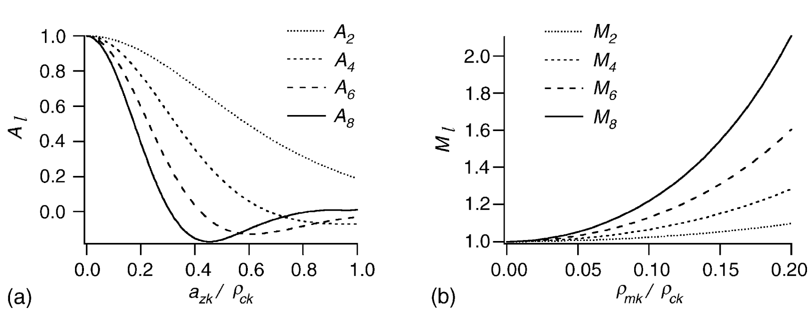

Fig. 2. Effect of: (a) finite axial amplitude a_{zk}, and (b) finite magnetron radius ρ_{mk}, of the outer ion with cyclotron radius ρ_{ck}, on the perturbations to the trap field expansion coefficients (see text).

where $\Omega_c = \Omega_E^2/\omega_c$. Likewise, the interaction of the ions' axial motions result in a second-order shift:

$$\Delta\omega_{zi}^{(2)} \cong -\Omega_z^2/[4(\omega_{zk} - \omega_{zi})]. \quad (11)$$

Unlike the "static" shifts, which for balanced ρ_{ck} cancel in determining the mass ratio, these shifts, since the sign depends on the relevant detuning, systematically perturb the measured ratio. However, in our present situation, for $\rho_{ck} \geq 1.2$ mm, with ions of fractional mass difference $>5 \times 10^{-4}$, these second order shifts in f_{ct} and f_z are $<10^{-14}$ and $<10^{-9}$, respectively, which are negligible. Moreover, these effects decrease as ρ_{ck}^{-6}.

3.3. Coupled magnetron motion

There is the possibility that the outer ion's large cyclotron motion, perhaps due to collisions with residual background gas molecules, could result in an increase in magnetron motion. Magnetron motion ρ_{mk} of the outer ion, cf. Eq. (9), leads to an induced magnetron motion of the inner ion $\rho_{mi} \sim \Omega_E^2\rho_{mk}/[\omega_{cti}(\omega_{mk} - \omega_{mi})]$. In contrast to the simultaneous two-ion technique [1–3] which requires strongly coupled magnetron motion, the magnetron frequencies of the two ions in our situation, for $\rho_{ck} > 1.2$ mm, are separated by shifts due to $B_2\rho_{ck}^2$ and $C_6\rho_{ck}^4$ that are >200 mHz, to be compared with $\Omega_E^2/2\pi\omega_{cti} <$ 16 mHz. Provided there is no gross excitation of the outer ion's magnetron motion, i.e., $\rho_{mk}/\rho_{ck} < 50\%$, this induced magnetron motion should be negligible.

4. Results

4.1. $^{13}C_2H_2^+/^{14}N_2^+$

Using our technique we obtained 28 sets of data, similar to Fig. 1, for the cyclotron frequency ratio $^{13}C_2H_2^+/^{14}N_2^+$, with ρ_{ck} varying from 0.8 to 2.0 mm. No systematic dependence on ρ_{ck} was evident, as would be expected if ion–ion interaction effects were significant. However, compared to the high-precision MIT result $R_{ref} = 0.999\,421\,460\,888$ (7), our weighted average ratio was $\Delta R = R - R_{ref} = 87\ (15) \times 10^{-12}$. The number in parentheses is the statistical error in our measurement, obtained from the errors of the simultaneous fit results of the individual runs; the reduced χ^2 our data was 3.5. The overall offset, and the large reduced χ^2 corresponding to larger-than-statistical variations between runs, imply significant systematic shifts. Our value for R also exhibited a time dependence, suggesting that the results may be sensitive to the details of the de-tunings between the various drive and respective ion frequencies, but in a way we do not currently understand.

4.2. $^{14}N_2^+/^{28}Si^+$

For $^{14}N_2^+/^{28}Si^+$ we combined a total of nine data sets obtained at $\rho_{ck} = 1.6$ and 2.0 mm. Our reference value is $R_{ref} = 0.998\,956\,584\,569$ (81) using the mass values in Ref. [20] (mainly derived from MIT data), corrected for electronic binding energies using the data in Refs. [21–23]. Our result

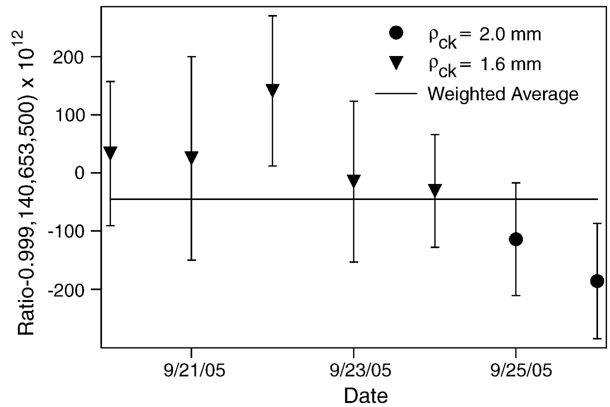

Fig. 3. Results for the cyclotron frequency ratio $^{28}SiH_3^+/^{31}P^+$. Each point is the result of a simultaneous fit to a ∼12 h run.

$\Delta R = R - R_{ref} = 76\ (29) \times 10^{-12}$, with reduced χ^2 1.9, agrees within the uncertainty of the reference value.

4.3. $^{28}SiH_3^+/^{31}P^+$

We chose $^{28}SiH_3^+$ as a reference for $^{31}P^+$ because this molecular ion, like CH_3^+ [24], is believed to have a planar-equilateral-triangular structure. Hence it should have no dipole moment that could produce a shift in cyclotron frequency as discussed in Ref. [2]. Fig. 3 shows our results for $^{28}SiH_3^+/^{31}P^+$, from which we obtain the ratio $M[^{28}SiH_3^+]/M[^{31}P^+] = 0.999\,140\,653\,455$ (44), statistical error only, with reduced $\chi^2 = 0.87$.

4.4. Mass of ^{31}P

Using the values of $M[^{28}Si]$ and M[H] from Ref. [20], and correcting for binding energies [21–23], we hence obtain $M[^{31}P] = 30.973\,761\,999\,7$ (14) (56) (19) (61)u, where we show in parentheses, our statistical error, our estimated systematic error, the error in the mass reference, and the total error, respectively. Since we are basing our new value for $M[^{31}P]$ on a single ratio and not several redundant ratios as in Ref. [13], and have not fully characterized the systematic errors, we have assigned a fractional systematic error of 1.8×10^{-10}, corresponding to twice the overall offset seen in the $^{13}C_2H_2^+/^{14}N_2^+$ data. Nevertheless our new result is 30 times more precise than the value in Ref. [20], $M[^{31}P] = 30.973\,761\,63$ (20)u. It agrees with the previous result within twice the previous error.

5. Conclusion

We have implemented a method for mass comparison of two ions simultaneously trapped in a Penning trap in which the ions are successively interchanged between the trap center and a large radius cyclotron "parking orbit". We have demonstrated that better than 10^{-10} statistical precision can be obtained using a single ion pair, and high statistical precision, $\sim 2 \times 10^{-11}$, can be obtained for the mass ratios in a few weeks of data acquisition. However, more investigation of systematic effects are required to exploit this statistical precision. We have obtained a significantly improved value for the mass of ^{31}P.

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