Editors' Suggestion

Deuteron-to-Proton Mass Ratio from Simultaneous Measurement of the Cyclotron Frequencies of H_2^+ and D^+

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By simultaneously measuring the cyclotron frequencies of an H_2^+ ion and a deuteron in a coupled magnetron orbit we have made an extended series of measurements of their cyclotron frequency ratio. From the observed changes in H_2^+ mass energy we have followed the decay of three H_2^+ ions to the vibrational ground state. We are able to assign some of our measured ratios to specific rovibrational levels, hence reducing uncertainty due to H_2^+ rotational energy. Assuming the most probable assignment, we obtain a deuteron-to-proton mass ratio, $m_d/m_p = 1.999\,007\,501\,272(9)$. Combined with the atomic mass of the deuteron [S. Rau *et al.*, Nature (London) **585**, 43 (2020).] we also obtain a new value for the atomic mass of the proton, $m_p = 1.007\,276\,466\,574(10)$ u.

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The most precise measurements of atomic mass ratios have been obtained by measuring cyclotron frequency ratios (CFRs) of single ions in cryogenic Penning ion traps [1–13]. Usually, but using a variety of techniques [1], the CFR is obtained by positioning one of the two ions to be compared at the center of the trap, measuring its cyclotron frequency, then replacing it with the second ion, measuring its cyclotron frequency, and then repeating. Despite considerable effort devoted to the stabilization of the magnetic field [5,14], and to methods for increasing the rate of interchange [9,15], variation of the magnetic field between the cyclotron frequency measurements limits the precision achievable for the CFR. An important exception was the technique developed at MIT [6,7,16], which is applicable to ion pairs whose masses are similar to within $\sim 10^{-3}$, in which the two ions are simultaneously trapped and then manipulated into strongly coupled magnetron orbits, such that the ions orbit the center of the trap, in the plane perpendicular to the magnetic field, 180° apart, and with a separation of ~1 mm. Simultaneous measurements of the (trap-modified) cyclotron frequencies of the two ions can then be carried out using the phase-coherent "pulse-and-phase" (PnP) technique [3]. In essence, a precision measurement of the CFR is reduced to a measurement of the difference in the cyclotron phases evolved by the two ions. This results in a suppression of the effect of temporal variation in the magnetic field on the CFR by 3 orders of magnitude, but also, because the ions follow similar paths through the magnetic and electrostatic fields, a suppression of certain systematic errors. These include the effects of shifts in the average position of the ions combined with linear magnetic field gradients, and effects that shift the axial frequency (which affect the mass ratio when using the invariance theorem to obtain the "true" cyclotron frequency [16,17]), such as ion-detector interaction.

However, this simultaneous method has only been applied to four mass ratios, all in the region of 30 u. Here, after a hiatus of nearly two decades, we report its first application to light ions, specifically to a determination of the deuteron-proton mass ratio, m_d/m_p, by measuring the CFR of H_2^+ to D^+. This work was also motivated by prospects for improved measurement of the proton-antiproton mass ratio (using H^-) in the noisy magnetic field environment of the antiproton decelerator at CERN [4,9]; and of the T-^{3}He mass difference [8], with application to antineutrino mass [18,19].

Mass ratios of hydrogen and helium isotopes are considered to be fundamental constants [2,20]. In the case of m_d/m_p new measurements are motivated by recent high-precision rotational and vibrational spectroscopy on trapped and sympathetically cooled HD^+ ions [21–23], and the parallel development of high-precision theory [24–26]. Assuming the validity of the theory, and making corrections for proton and deuteron charge radii, the comparison between theory and spectroscopy yields the quantities $R_\infty[m_e(1/m_p + 1/m_d)]$ and $R_\infty[m_e(1/m_p + 1/m_d)]^{1/2}$ for rotational and vibrational transitions, respectively. Conversely, if these quantities are obtained from other measurements, the comparison can be used to test QED theory and search for physics beyond the standard model [27]. In either case, a sufficiently precise value for m_d/m_p is needed to link the above quantities to the electron-proton mass ratio, m_e/m_p. Since m_e/m_p (or m_e/m_d) links the electron mass to atomic masses [28], m_d/m_p also potentially impacts atom-recoil determinations of the fine structure constant that require precise values of $m_e/m_{\rm Rb}$ and m_e/m_{Cs} [29,30].

Measurement of the CFR of H_2^+ to D^+ has advantages for obtaining m_d/m_p in that H_2^+ and D^+ form a mass doublet (fractional mass difference 7×10^{-4}) reducing many systematic errors. It also allows application of the simultaneous measurement technique we use here. A major complication is that the H_2^+ can be created in one of a large number of rovibrational levels, with lifetimes against spontaneous $E2$ decay of order one week. The H_2^+ then cascades into one of several rotational levels of the vibrational ground state. These rotational levels have lifetimes of many months or years, too long to expect further decay, but whose mass energy must still be taken into account at the desired precision. (For example, rotational levels $N = 1$, 2, 3, 4 of $v = 0$ are shifted relative to $N = 0$ by fractional mass increases of 3.8, 11.5, 22.9 and 38.0×10^{-12}, respectively, and $v = 1$, $N = 0$ by 1.45×10^{-10} [31]). In a previous measurement of the H_2^+/D^+ CFR [12] we used a technique in which the ions were simultaneously trapped, but alternated between the trap center and a 2 mm radius "parking" cyclotron orbit [32]. With that method we were able to partly resolve vibrational levels. Further, by using Stark quenching, which significantly increased the rate of H_2^+ vibrational decay in the large cyclotron orbit [33], we were able to measure the H_2^+/D^+ CFR with several different H_2^+ ions, knowing them to be in the vibrational ground state. However, we were not able to determine the rotational state. Hence, in our previous work [12], to determine an average correction for ground state rotational energy, we used a simulation that assumed an initial rotational distribution, together with an analysis based on the observed scatter of the CFRs.

Here, in contrast to our previous work, the H_2^+ ions were not placed in large cyclotron orbits and so did not undergo significant Stark quenching. But also, since both ions in their coupled magnetron orbits were displaced by 0.4 mm from the center of the trap, they were not exposed to the tenuous molecular beam of background gas that continuously enters our Penning trap through a 0.5 mm diameter hole in the upper end cap [1]. This increased the ion lifetime against collision with a neutral molecule from a few days to several months or longer. Hence, we could perform measurements with the H_2^+ in a single vibrational level with higher precision and over a longer duration. By least-squares fitting the theoretical rovibrational energy differences [31,34] to our CFR data for three H_2^+/D^+ ion pairs, we were able to assign some of our measured ratios to specific rovibrational levels. Assuming our assignment is correct, this removes the uncertainty on the H_2^+/D^+ CFR due to rotational energy.

Method.—The measurements used the 8.5 T hyperboloidal-electrode Penning trap described previously [1]. Only the axial motions of the ions were detected and resistively cooled, which was done using a superconducting circuit (with resonance near 688 kHz and quality-factor 35 000), coupled to a dc SQUID. The cyclotron motions were detected and cooled by coupling them to the axial motion using tilted quadrupole rf drives [35]. The D^+ and H_2^+ ions were both produced in the trap by electron beam ionization as in Ref. [12]. Unwanted ions were removed by mass-selective axial excitation. The D^+ was made first and then excited to a 1.5 mm radius cyclotron orbit. The H_2^+ was made inside the D^+ orbit and then driven into a magnetron orbit of radius about 0.6 mm. The cyclotron motion of the D^+ was then reduced by cyclotron-to-axial coupling, resulting in a H_2^+/D^+ ion pair with a coupled magnetron motion. As discussed in Refs. [16,36], this motion can be described as the sum of a "separation mode" $\vec{\rho}_{\rm sep} = \vec{\rho}_2 - \vec{\rho}_1$ and a "common mode" $\vec{\rho}_{\rm com} = (\vec{\rho}_2 + \vec{\rho}_1)/2$ (with amplitudes $\rho_{\rm sep}$, $\rho_{\rm com}$), where $\vec{\rho}_1$, $\vec{\rho}_2$ are vectors representing the positions of the H_2^+ and D^+ in their magnetron orbits. $\vec{\rho}_{\rm com}$ rotates at a frequency very close to the average of the single-ion magnetron frequencies, which is near 3.64 kHz. Because of ion-ion Coulomb interaction, $\vec{\rho}_{\rm sep}$ rotates at a slightly higher frequency than $\vec{\rho}_{\rm com}$, by $\Omega_m/2\pi = e/(4\pi^2\varepsilon_0 B\rho_{\rm sep}^3)$, where B is the magnetic field, and e and ε_0 have their usual meanings. This causes the ions to alternately spiral towards and away from the trap center with a period ~10 s, the extent of the inward and outward motion depending on $\rho_{\rm com}$. Using the methods described in Ref. [36] this swapping motion was monitored and reduced, and $\rho_{\rm sep}$ modified as necessary, till we achieved a $\rho_{\rm sep}$ between 0.79 and 0.82 mm and $\rho_{\rm com} < 0.03$ mm.

Having positioned the ions in a coupled magnetron orbit we then set up runs to measure the CFR using the PnP technique [3] simultaneously on both ions. For the PnP measurements the trap ring-to-endcap voltage was set so that the axial frequencies of the H_2^+ and D^+ were symmetric about the detector resonance. Before each PnP, the ions' axial motions were cooled by shifting the trap voltage to bring each ion alternately to resonance. While still on resonance, cyclotron-to-axial coupling pulses were applied to cool the cyclotron motion. For the majority of the measurements a cyclotron drive time (CDT) of 5 ms was used, producing a cyclotron radius of approximately 21 μm. CDTs of 6, 9, and 12 ms were also used to quantify systematic errors due to special relativity (SR) and other amplitude dependent effects. A run typically lasted 6 h and consisted of 240 PnPs with phase-evolution-time ($T_{\rm evol}$) of 10.1 s, interleaved with PnPs with $T_{\rm evol}$ of 0.1, 0.3, 1.1, 3.1 s for phase unwrapping. After the run we manually checked for an increase in $\rho_{\rm com}$ and reduced it if necessary.

In contrast to the MIT work at ~30 u [6,36,37], for mass-2 ions the main source of noise on the cyclotron frequency difference (in addition to detection phase noise) was SR combined with variation in the ions' cyclotron radii from PnP to PnP. The main component of these cyclotron

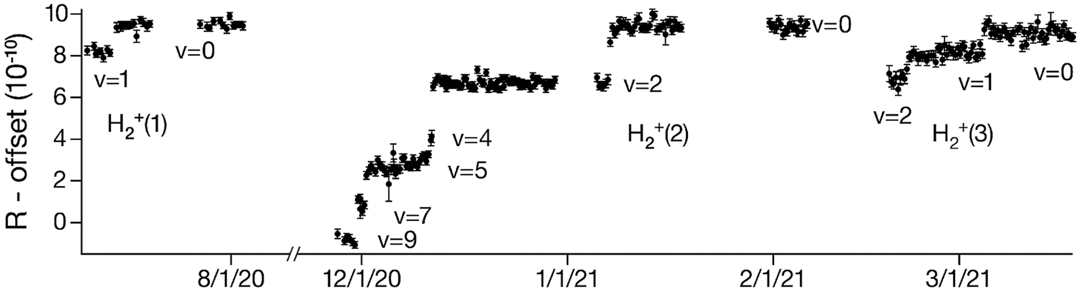

FIG. 1. H_2^+/D^+ cyclotron frequency ratio measurements using three different H_2^+ ions. The data are for 5 ms cyclotron drive time, except for $H_2^+(1)$, $v = 1$, where data at 6 ms have been corrected to 5 ms. The offset is 0.999 231 659.

radius variations was the initial "thermal" cyclotron motion before the cyclotron drive pulse of the PnP. This thermal cyclotron motion is the result of adiabatic action transfer from the axial motion by the cyclotron-to-axial coupling pulses [35], ideally resulting in a cyclotron temperature of $T_c = (f_{ct}/f_z)T_z$, where f_z and f_{ct} are the ions' axial and trap-modified cyclotron frequencies, and T_z is the axial temperature. In order to reduce T_c we reduced T_z by applying feedback to the axial motion of each ion when on resonance with the detection circuit [38]. With axial feedback we were able to reduce T_c, as determined from noise on the cyclotron frequency, by a factor of 2. The lowest noise on f_{ct} corresponded to $T_z \leq 3$ K. Nevertheless, because the SR noise on f_{ct} was comparable to the noise from magnetic field variation in our alternating measurements [12], the gain in resolution per run on the CFR was only slightly more than a factor of 2, and partly a result of the increase in the number of long T_{evol} PnPs per unit time. This contrasts with the dramatic gain in precision obtained in a more magnetically noisy environment at mass-30 [6]. Our detection phase noise varied and degraded throughout the data taking, apparently due to an increase in external electromagnetic interference.

Data and analysis.—To obtain the CFR corresponding to a run we averaged the phases from the PnPs over the whole run, both for each ion separately, and for the difference between the ions. For most runs the individual ion's cyclotron phases could be unwrapped to $T_{\mathrm{evol}} = 10.1$ s; this enabled a consistency check for the phase unwrapping. Fitting straight lines to the unwrapped phases versus T_{evol} then gave the trap-modified cyclotron frequencies f_{ct1}, f_{ct2} for the H_2^+ and D^+, respectively, and their difference $f_{ct2} - f_{ct1}$. Together with the averages of the axial frequencies f_{z1}, f_{z2}, obtained at the end of the PnPs, $f_{ct2} - f_{ct1}$, f_{ct1} and f_{ct2} were then inserted into Eqs. 5.6 and 5.9 of Ref. [36] to yield the CFR. We note that the uncertainty on the CFR is essentially given by the uncertainty in $f_{ct2} - f_{ct1}$.

Over the whole data taking campaign we made three H_2^+ ions and followed their decay to the ground vibrational state by repeated measurements of the H_2^+/D^+ CFR. The raw CFRs (results of each run) for the three ion pairs are shown in Fig. 1. Our procedure for assigning the measured CFRs to specific H_2^+ rovibrational levels was as follows. First, (after correcting some data not taken at 5 ms CDT to allow for SR and cyclotron radius imbalance, see the discussion of systematic corrections below), we grouped the results in each plateau of Fig. 1 to obtain an average CFR corresponding to a single level. (To allow for the possibility that the transition may have occurred within one of the runs, before or after the apparent jump in run-averaged CFR, we repeated the analysis with these points removed. There was no significant difference in the final results.) This resulted in 11 averaged ratios, $R_i, i = 1, 2...11$, with statistical uncertainties σ_i, to be assigned to rovibrational levels: specifically 2 for $H_2^+(1)$, 6 for $H_2^+(2)$, and 3 for $H_2^+(3)$. The σ_i were determined from the uncertainties in the CFR results of the individual runs, which derive from the standard deviations of the phase measurements in each run. We then carried out a least-squares fit of the accurately known H_2^+ rovibrational level spacings [31,34] to our R_i by minimizing the overall χ^2,

$$\chi^2 = \sum_{i=1}^{11} \{[R_i - R_{00}(5\ \mathrm{ms}) - \Delta R(v_i, N_i)]/\sigma_i\}^2, \quad (1)$$

where $\Delta R(v_i, N_i)$ is the calculated shift in the CFR due to the extra energy corresponding to vibrational level v_i and rotational level N_i; and $R_{00}(5\ \mathrm{ms})$, the only free parameter, is the H_2^+/D^+ CFR corresponding to H_2^+ in $v = 0$, $N = 0$, and with 5 ms CDT (and as yet uncorrected for systematics). Small corrections for H_2^+ polarizability are also included in $\Delta R(v_i, N_i)$ [39,40]. A search over all likely assignments $\{(v_i, N_i)\}$ was carried out, subject to the electric-quadrupole selection rules for H_2^+ vibrational decay, $\Delta N = 0, \pm 2, N = 0$ does not go to $N = 0$, in each case finding the minimum χ^2 by varying $R_{00}(5\ \mathrm{ms})$.

In Fig. 2 we show the resulting minimum χ^2 and $R_{00}(5\ \mathrm{ms})$ for all such $\{(v_i, N_i)\}$ assignments giving a total χ^2 less than 40, with different markers used to indicate whether each H_2^+ ion has N even or odd. (A well-separated group centered at higher R_{00} can be rejected because these assignments require an unreasonably large initial N, ≥ 7, for one or more of the ions [41,42].) The assignments

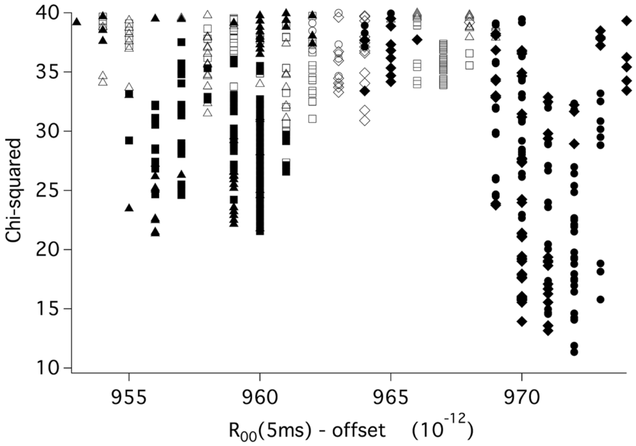

FIG. 2. Minimum chi-squared with respect to $R_{00}(5\ \mathrm{ms})$, with a step size of 10^{-12}, for assignments of rovibrational levels to our averaged CFRs. The markers indicate whether the N values for the three H_2^+ ions are odd or even as follows: solid round *ooo*, solid diamond *eoo*, solid square *eee*, solid triangle *oee*; open round *oeo*, open diamond *eeo*, open square *eoe*, open triangle *ooe*.

below $\chi^2 = 31$ can be separated into three groups centered on different $R_{00}(5\ \mathrm{ms})$. More specifically, in the highest R_{00} branch (solid rounds and solid diamonds with $R_{00}(5\ \mathrm{ms}) - \mathrm{offset} \geq 969 \times 10^{-12}$), all assignments up to χ^2 of 33 have $H_2^+(2)$ and $H_2^+(3)$ both odd. Moreover, in this branch the third and last two levels of $H_2^+(2)$ are always (5,5), (2,3), and (0,3), respectively; and the last two of $H_2^+(3)$ always (1,3) and (0,5), respectively. In the two lower (closely spaced) R_{00} branches (solid squares and solid triangles with $R_{00}(5\ \mathrm{ms}) - \mathrm{offset} \leq 961 \times 10^{-12}$), the likely assignments have $H_2^+(2)$ and $H_2^+(3)$ both even, with the third and last levels of $H_2^+(2)$ being (5,4) and (0,2), respectively; and the last two of $H_2^+(3)$ being (1,2) and (0,4), respectively. The two lower branches are split according to whether the penultimate level of ion-2 is (2,0) or (2,2). We continue the analysis using only these 5 ratios that can be uniquely assigned, and so uniquely corrected for rovibrational energy within these three groups. From the weighted averages of the 5 corrected R_i we obtain $R_{00}(5\ \mathrm{ms}) = 0.999\,231\,659\,971\,2(21), \ldots 659\,958\,9(29)$, and $\ldots 659\,955\,0(27)$, with statistical uncertainties given in parentheses. Further, we estimate the relative probabilities of these three $R_{00}(5\ \mathrm{ms})$ (in order of highest to smallest R_{00}) as lying between $1{:}0.012{:}0.058$ and $1{:}0.13{:}0.27$. More details are given in the Supplemental Material [43].

A summary of the corrections we apply to $R_{00}(5\ \mathrm{ms})$ to account for systematic shifts is given in Table I. As in Ref. [12], the largest systematic shift is due to SR and imbalance in the cyclotron radii, produced by the nominally identical, but different frequency, cyclotron drive pulses at the start of the PnPs. To obtain the required correction for 5 ms CDT we plot CFRs for a given rovibrational state versus CDT^2 and extrapolate to zero. (We note that the 6 ms CDT data were not used in obtaining our final results, and the correlation between our quoted statistical uncertainty and uncertainty in this imbalance correction is negligible.) While this procedure allows for imbalance in the cyclotron radii produced by the cyclotron drive pulse, it does not allow for possible imbalance in the average "thermal" cyclotron energy of the H_2^+ and D^+ before the pulse, which also contributes to the cyclotron energy during the cyclotron phase evolution. As discussed above, this initial cyclotron energy, $k_B T_c$, also contributes to the noise on f_{ct}. Hence, we attempted to quantify any imbalance in T_c by using the Allan variances of the phases of the H_2^+ and D^+ PnPs to estimate a difference in the noise on f_{ct1} and f_{ct2}. Because this procedure is subject to other noise, we applied this correction with an uncertainty equal to 100% of the correction. (This corresponds to a difference in T_c equivalent to a 0.66 K difference in T_z). This is the largest systematic uncertainty. Remarkably, due to the symmetry between the ions, ion-ion Coulomb interaction shifts the CFR by less than 10^{-13} and the combined effect of trap imperfections is less than 10^{-12}. Details are given in the Supplemental Material [43].

TABLE I. Systematic corrections to the H_2^+/D^+ CFR. These apply to measurements with cyclotron drive times of 5 ms.

Source	Correction (10^{-12})
Spec. Rel. and imbal. in driven cyc. radii	29.5(1.4)
Spec. Rel. and imb. in thermal cyc. radii	2.9(2.9)
Ion-ion interaction	< 0.1
Trap imperfections, imb. in mag. radii	$-1.1(0.2)$
Trap imperfections, imb. in axial amps.	0.5(0.5)
Total systematic correction	31.8(3.7)

Results.—Combining the most likely value of $R_{00}(5\ \mathrm{ms})$ with the systematic corrections in Table I, we obtain for the $H_2^+(0,0)/D^+$ CFR (the inverse of the mass ratio), $R_{00} = 0.999\,231\,660\,003\,0(21)(37)(43)$, where the numbers in parentheses are the one-sigma uncertainties due to statistics, systematics, and the total uncertainty, respectively. From this, using the H_2^+ ground state binding energy from Ref. [24] and m_e from Ref. [20], and without any significant increase in uncertainty, we obtain $m_d/m_p = 1.999\,007\,501\,272(9)$. (However, we note that this value

TABLE II. Result for m_d/m_p compared with previous values.

Source	m_d/m_p
This work	1.999 007 501 272(9)
Fink and Myers 2020 [12]	1.999 007 501 274(38)
Rau *et al.* 2020 [13]	1.999 007 501 228(59)
CODATA 2018 [20]	1.999 007 501 39(11)

TABLE III. Result for m_p compared with previous values.

Source	m_p (u)
This work and Rau *et al.* [13]	1.007 276 466 574(10)
Heisse *et al.* [11]	1.007 276 466 598(33)
CODATA 2018 [20]	1.007 276 466 621(53)

shifts down by 2.7 or 3.6 sigma if one of the less likely assignments is chosen.) In Table II our most probable result is compared with our previous measurement [12], the value obtained by Rau *et al.* [13] from measurements of the atomic masses of D^+ and HD^+ combined with the proton mass of Ref. [11], and the value from the 2018 CODATA fundamental constants. As can be seen, our new result is in good agreement with the previous results, but has an uncertainty smaller by factors of 4, 6 and 12, respectively. Combining our new value for m_d/m_p with m_d from [13], viz. $m_d = 2.013\,553\,212\,535(17)$ u, obtained by measuring the deuteron against $^{12}C^{6+}$, we obtain a mass for the proton with uncertainty of 1.0×10^{-11}. In Table III this result is compared with the direct measurement of the proton against $^{12}C^{6+}$ of Heisse *et al.* [11], and the 2018 CODATA value, and seen to be in good agreement.

Conclusion.—The method of simultaneous measurement of cyclotron frequencies of two ions in coupled magnetron orbits has been re-developed and applied to the light ions H_2^+ and D^+. This enabled sufficient mass resolution to assign certain measured CFRs to one of two H_2^+ rovibrational states with high probability, and to single states with a probability of more than 2.5 to 1. If we assume the most probable identification we obtain a deuteron-to-proton mass ratio with fractional uncertainty of 4.5×10^{-12}. Combined with the deuteron mass of Rau *et al.* this yields a value for the proton mass with fractional uncertainty of 1.0×10^{-11}.

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[43] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.127.243001 for additional information on obtaining $R_{00}(5\text{ ms})$ and the systematic corrections.