Deuteron-to-Proton Mass Ratio from the Cyclotron Frequency Ratio of H_2^+ to D^+ with H_2^+ in a Resolved Vibrational State

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We have measured cyclotron frequency ratios of H_2^+ to D^+ with sufficient precision to resolve the mass increase of H_2^+ due to vibrational energy. Additional discrimination against excited vibrational levels was provided by increasing the rate of vibrational decay through Stark-quenching. From our results we obtain a value for the deuteron-to-proton mass ratio, $m_d/m_p = 1.999\ 007\ 501\ 274(38)$, which has an uncertainty three times smaller than the current CODATA value.

The deuteron-to-proton mass ratio m_p/m_d is generally regarded as a fundamental constant [1, 2]. Along with the proton-to-electron mass ratio [3–5], m_d/m_p is required for the determination of the Rydberg constant R_∞ and the proton and deuteron mean-square charge radii r_p and r_d, from combined analysis of precision spectroscopy of hydrogen and deuterium [6–8]. A high precision value of m_d/m_p is also needed to enable developing theoretical calculations for transition energies in H_2^+, HD^+ and D_2^+ [9–11] to be compared with experiment [12, 13]. In the future, such comparisons should provide a competitive method for obtaining R_∞, r_p and r_d [14, 15]. This has an increased importance due to discrepancies between values for r_p and r_d obtained from spectroscopy on muonic versus electronic hydrogen [16]. Additionally, the quantity $(m_d/m_p - 1)m_p$, combined with the deuteron binding energy [17, 18], yields the neutron mass.

The current CODATA value for m_d/m_p [2] is largely based on the atomic mass of the deuteron from Zafonte and Van Dyck [19] and the atomic mass of the proton from Heisse *et al.* [4, 5], obtained by measuring cyclotron frequency ratios (CFRs) of d and p against highly-charged ^{12}C ions. Such measurements are necessarily prone to systematic effects due to the difference in mass and charge of the ions being compared – for example, different image charge shifts and different anharmonic shifts [20], and require specially engineered Penning traps to mitigate them [5]. By contrast, measurement of the H_2^+/D^+ CFR has the advantage that such systematics largely cancel, because the ions have the same charge and the fractional difference in their masses is $< 10^{-3}$. This reduction in systematic effects was exploited in the previous measurement of the H_2^+/D^+ CFR by Solders *et al.* [21], who used a Penning trap with the ion-destructive and lower mass resolution time-of-flight detection technique. However, when H_2 is ionized by electron impact, the increase in equilibrium nuclear separation results in the H_2^+ being formed in any of 20 bound vibrational levels [22], although with 90% probability in $v \leq 6$ [23, 24], all of which are highly metastable [25, 26]. Because of the relatively high energy separation of the vibrational levels, this results in a significant shift of the average mass of the H_2^+ ions. For instance, between $v = 0$ and $v = 1$ the mass increases by about 1.4×10^{-10}. In ref. [21] these mass differences were completely unresolved, so the authors corrected their measured CFR by assuming the H_2^+ ions had a vibrational distribution as determined from photo-dissociation measurements [23, 24].

TABLE I. Mean lifetimes τ (days) against spontaneous decay [25, 26] SP, and against spontaneous decay and Stark-quenching (SP+SQ) [31], for an H_2^+ ion in a 2 mm radius cyclotron orbit in a 8.5 tesla magnetic field. These values are for rotational quantum number $N = 0$, but the variation with N is small.

Initial v	1	2	3	4	5	6	7	8
τ (SP)	22.2	12.5	9.4	8.0	7.2	6.8	6.6	6.6
τ (SP+SQ)	2.13	0.86	0.46	0.27	0.16	0.10	0.06	0.04

Here we report measurements of the CFR of H_2^+ to D^+ using single-ion, cryogenic Penning trap techniques [27–29] with enough precision to clearly resolve the different vibrational levels of H_2^+. To our knowledge this is the first time that the mass increase of a molecule due to vibrational energy has been directly observed [30]. Our CFR measurements also demonstrate and make use of the increased rate of vibrational decay of H_2^+, resulting from the strong motional electric field an ion experiences in a large radius cyclotron orbit [31] – an effect which may have application to optical and microwave spectroscopy of the antihydrogen molecular ion [32]. Because of the enhanced decay, see Table I, we were able to ensure an H_2^+ was in the vibrational groundstate by simply storing it for sufficient time in a 2 mm radius cyclotron orbit.

Our final result for m_d/m_p was hence limited by uncertainty in the average rotational energy and not the vibrational energy of the H_2^+. It improves on the CODATA 2018 [2] value by a factor of 3 and on the result of Solders *et al.* [21] by a factor of 9. Assuming the validity of the recent proton mass measurement [5], our result indicates a lighter deuteron mass, by $1.6(9) \times 10^{-10}$ u, than that reported in [19]. This new deuteron mass reduces, but does not eliminate the $> 4\sigma$ discrepancy in the $m_p + m_d - m_h$ mass difference discussed in [5, 33, 34].

Method.– Since the techniques are similar to those used in our previous light ion measurements [30, 33, 35] they are only described briefly here. The CFR measurements were made using pairs of H_2^+ and D^+ ions, simultaneously trapped in a Penning trap with hyperboloidal electrodes and maintained at 4.2 K [20], immersed in a carefully shimmed 8.5 tesla magnetic field. The measurement of the cyclotron frequency was carried out on an ion centered in the trap using the phase-coherent Pulse-and-Phase method [28], while the other ion was in a 2 mm radius cyclotron orbit [36]. After a cyclotron frequency measurement on the centered ion, the ions were interchanged and the cyclotron frequency of the second ion was measured, and so on. For our longest runs, which took up to 7 hours, this gave up to 15 alternating measurements on each ion, resulting in a CFR with statistical uncertainty of about 35×10^{-12}.

D^+ ions were made in the trap from a tenuous few-ms-pulsed beam of CD_4 injected into the top of the cryogenic insert and directed at the Penning trap 2 m below. A fraction of this beam entered the Penning trap through a 0.5 mm diameter hole in the center of the upper end-cap electrode. The pulse of CD_4 was coincident with the biasing of a field-emission point (FEP) to 700 V, producing a few nA electron beam which entered the Penning trap through a 0.5 mm diameter hole in the lower end-cap. Since this method of ion making resulted in some degradation of the vacuum, H_2^+ ions were made by simply running the FEP for several seconds with no gas injected. Some H_2^+ may have been produced from background H_2 from the top of the cryogenic insert, which was at room temperature. This gas also forms a very weak but continuous molecular beam, entering the trap through the hole in the upper end-cap. However, H_2^+ were also likely produced from H_2 desorbed by the electron beam from cryogenic surfaces. The average ion lifetime (presumably against ion-neutral reaction) was over a month for an ion in a 2 mm cyclotron orbit, but, for an ion in the trap center, varied from ~ 10 to ~ 2 days as the experiment progressed, with no obvious difference between D^+ and H_2^+.

Most of the H_2^+/D^+ CFR measurements were made with an inner ion cyclotron radius of 20 μm. However, radii of 15 to 50 μm were used to study amplitude-dependent systematic shifts to the CFR due to special relativity and trap field imperfections. These shifts were also studied with runs using a single ion at 15 and 35 μm cyclotron radii. A shift to the CFR due to a possible change in equilibrium position between the H_2^+ and D^+ ions was quantified by measuring the non-mass-doublet CFRs H_3^+/H_2^+ and $^3He^+/H_2^+$. Runs with a single ion were also used to study the small shift in the CFR due to ion-detector interaction. Many other measurements with single ions were used to characterize the electrostatic potential and the magnetic field [37].

Data and Analysis.– In total, CFR measurements were obtained from 83 H_2^+/D^+ runs with 27 different H_2^+ ions. These runs can be categorized into: a) series of runs made with an H_2^+ ion that had been made previously, and stored in a large radius cyclotron orbit for more than 12 days, and so could confidently be assumed to be in $v = 0$ before measurements started, b) series of runs in which an attempt was made to follow the decay from a high v level to $v = 0$, with results consistent with Stark-quenching, but only once successfully retaining both ions till decay to $v = 0$ had occurred, c) single, often short runs where an H_2^+ ion was made and the H_2^+/D^+ CFR measured, but since the H_2^+ was found to be in a high v, it was removed and then replaced with a newly made ion, and d) series of runs in which, from the first measurement, the H_2^+ was determined to be very likely in either $v = 1$ or $v = 0$, and was then retained for repeated measurements. In Fig. 1 the results of all successful runs for all ions are plotted as a histogram with respect to the measured ratio, uncorrected for systematics. This histogram shows resolved peaks corresponding to H_2^+ in $v = 0$, 1 and 2, but not for ions in higher vibrational levels. Besides low statistics, this can be explained as due to the high probability for H_2^+ vibrational decay occurring during the run due to Stark-quenching, see Table I.

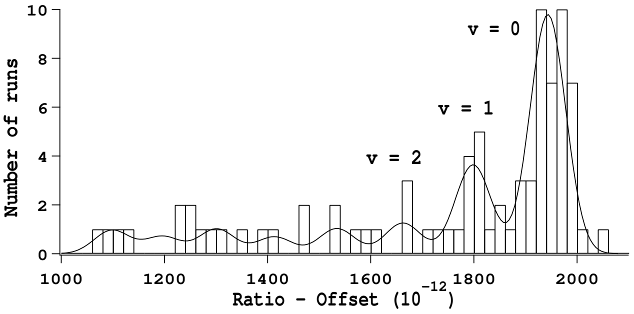

FIG. 1. Histogram of the results of 83 runs for the H_2^+/D^+ cyclotron frequency ratio (uncorrected for systematics) obtained with 27 different H_2^+ ions. The fit, which was not used for our final results, consists of the sum of 8 Gaussians with centroid spacing fixed by the known energy separation between the different vibrational levels of H_2^+ (for $N = 0$), with floating peak heights. The lack of correspondence between the fit and data for higher v is consistent with the H_2^+ ions decaying during a run. The offset is 0.999 231 657 985.

Obtaining an average CFR corresponding to an H_2^+ in $v = 0$ from fits to the histogram in Fig. 1 involves issues of binning and the asymmetrical blending of the peaks for different v. It also discards information provided by the uncertainties of each run result and the history of the H_2^+ decay. Instead, for determining the average $H_2^+(v = 0)/D^+$ CFR, we selected sequences of runs corresponding to seven ions, believed to be in $v = 0$, from only the above categories a) and d). Specifically, these consisted of three sequences of runs using three "old" ions, that is H_2^+ ions that had been stored for more than 12 days in a 2 mm cyclotron radius orbit and so were known to be in $v = 0$ at the start of the CFR measurements; three sequences of runs using "new" ions, where the H_2^+ ion was apparently made in $v = 0$ as determined from the first run; and one sequence where the ion was possibly in

TABLE II. Corrections $\Delta R(N)$ to the H_2^+/D^+ CFR (in units of 10^{-12}), and occupation probability estimates $P(N)$, for rotational levels of $H_2^+(v=0)$, assuming an initial H_2 rotational temperature of 300 K. "$P(0,N)$", H_2^+ formed in $v=0$; "$P(Cas,N)$", H_2^+ formed in excited vibrational levels with a distribution as given by [23] cascading to $v=0$.

N	0	1	2	3	4	5	6	7
$\Delta R(N)$	0	3.8	11.5	22.9	38.0	56.7	78.7	104.0
$P(0,N)$	0.132	0.665	0.115	0.084	0.003	0.001	0.000	0.000
$P(Cas,N)$	0.056	0.385	0.130	0.284	0.054	0.075	0.008	0.008

$v=1$ during the first run, but was subsequently in $v=0$ for remaining runs. In these last 4 sequences the first run was also rejected. This reduces the probability to a negligible level that the first run of the remaining "$v=0$ sequence" was an outlier for an ion actually in $v=1$, or that the ion decayed from $v=1$ to $v=0$ during this run. More details are given in the supplementary material. The $1/\sigma^2$ weighted averages for these seven run sequences, uncorrected for systematics, are shown in Fig. 2.

Correction for Rotational Energy.– The results displayed in Fig. 2 can be averaged to give an uncorrected grand average for the H_2^+/D^+ CFR of 0.999 231 659 939, with statistical uncertainty of 6.3×10^{-12}. However, the mean lifetimes of the lower rotational levels of $H_2^+(v=0)$ are much greater than the timescale of our experiment even with Stark-quenching [31]. Hence, allowance must be made for the rotational energy of the H_2^+ [26]. The corrections to be made to a measured H_2^+/D^+ CFR, with the H_2^+ ion in a state with $v=0$ and rotational quantum number N, to obtain the CFR corresponding to $N=0$, are given in the first row of Table II.

To obtain an initial estimate of the correction to be applied to our average CFR, we assume that the rotational distribution of the H_2^+ resulting from electron impact ionization of H_2 will be similar to that of the parent H_2 [23, 38]. For the case of H_2^+ ions made directly in $v=0$, if the parent H_2 originates from background gas at temperature T, it follows that the rotational distribution of the H_2 ions will be given by the Boltzmann distribution $P(N)\propto(2I+1)(2N+1)e^{-E(N)/k_BT}$, where $P(N)$ is the probability of both the parent H_2 and daughter H_2^+ occupying rotational level N, $E(N)$ is the rotational energy of H_2 in rotational level N, and the total nuclear spin I is either 0 or 1, depending on whether N is even or odd. This probability distribution is given in the second row of Table II for $T(H_2)=300$ K, corresponding to H_2 from the top of the insert. For the case of H_2^+ ions made in (unknown) excited vibrational levels and then allowed to decay to $v=0$, we assume an initial vibrational distribution as given in [23], with the distribution over N given by the above Boltzmann distribution. We then calculated the resulting rotational distribution in $v=0$ by modeling the ro-vibrational cascade using branching ratios obtained by combining the spontaneous decay rates of [25] with the Stark-quench rates of [31]. As can be seen from the last row of Table II, the cascade causes the rotational distribution to broaden and shift to higher N. Using this model, and assuming an initial H_2 rotational temperature of 300 K, the average corrections for rotational energy are 6.0, 12.1 and 17.3×10^{-12}, for ions made in $v=0$, $v=1$, or distributed according to [23], respectively. The corresponding correction to the average of the data in Fig. 2 is $12(2)\times10^{-12}$. For H_2^+ formed from hydrogen desorbed from cryogenic surfaces we do not know the rotational distribution. However, when H_2 is produced by the highly exothermic process of recombination of H atoms on cryogenic surfaces [39, 40], effective rotational temperatures $<\sim$300 K have been observed. This suggests that 300 K is a reasonable *upper* estimate of the average rotational temperature of the parent H_2 of the H_2^+ ions in our Penning trap, whatever its source.

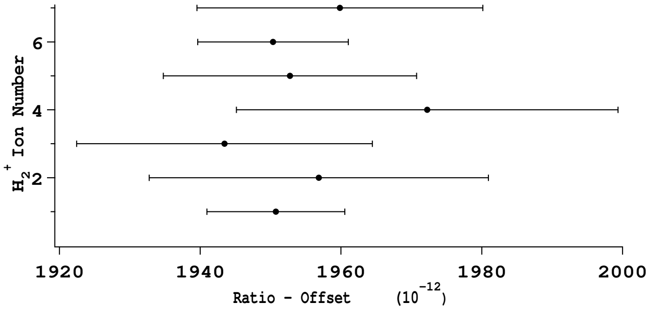

FIG. 2. Average H_2^+/D^+ CFRs (uncorrected for systematic effects) for the sequences of runs with H_2^+ ions in $v=0$ used to obtain our final result. The error bars are the one-sigma statistical uncertainties. The offset is 0.999 231 657 985 as in Fig. 1. H_2^+ ions 1, 3 and 4 had been stored in a 2 mm radius cyclotron orbit for more than 12 days before measurements; ions 2, 5 and 7 were most likely made in $v=0$, ion 6 in $v=0$ or $v=1$. The number of runs used to form the averages for ions 1,2 ..7 are 13, 2, 2, 2, 4, 8, and 2, respectively.

In order to estimate the average correction for H_2^+ rotational energy without assuming an initial rotational temperature, we carried out a Bayesian maximum likelihood estimation (MLE) that makes use of the scatter of the data points in Fig. 2. This resulted (see supplementary material) in a correction for average rotational energy of $10.7(10.7)\times10^{-12}$. An additional concern is that during a sequence of runs N could increase due to collisions. To attempt to quantify this we fitted straight lines to the run sequences used to give the data in Fig. 2, to search for any overall increase or decrease of the ratio with respect to time spent at the center of the trap. Averaged over all 7 ions, the difference between the overall average ratio, $\langle R\rangle$, and the average of the $t=0$ intercepts, $\langle R(0)\rangle$, was $\langle R\rangle-\langle R(0)\rangle=-5.1(12.4)\times10^{-12}$. Although this is not statistically significant evidence for rotational heating, to be conservative we combine this with our result from the MLE to obtain a total correction for rotational energy of $15.8(16.4)\times10^{-12}$. (Although the correction

TABLE III. Systematic corrections and uncertainties applied to the average H_2^+/D^+ CFR.

Source	Correction(10^{-12})
Statistics	0.0 (6.3)
H_2^+ Rotational energy	15.8(16.4)
Imbalance in cyclotron radii	40.7 (7.2)
Ion-detector interaction	8.2 (1.0)
Shift in average ion position	−0.6 (0.6)
H_2^+ Polarizability	1.1 (0.3)
Total	65.2(19.0)

TABLE IV. Our result for m_d/m_p compared with previous values.

Source	m_d/m_p	Other-This work(10^{-11})
This Work	1.999 007 501 274(38)	–
Refs. [5, 19]	1.999 007 501 432(77)	15.8(8.6)
Ref. [21]	1.999 007 500 72(36)	−55(36)
CODATA-18	1.999 007 501 39(11)	12(11)

cannot be negative we let the error bar be symmetrical for simplicity.)

Other Systematic Corrections and Uncertainties.– In Table III we summarize all the systematic corrections and uncertainties we apply to our average H_2^+/D^+ CFR. The largest correction is due to the difference in the cyclotron radii of the two ions for the same nominal cyclotron drive voltage and pulse duration, due to the frequency dependence of the transfer function, combined with special relativity and trap field imperfections. The other significant correction is from the shift to the axial frequency (and hence cyclotron frequency when using the invariance theorem [27]) due to ion-detector interaction. This was obtained using the model in [41] combined with measurements of the frequency width of the ion's axial signal, and confirmed by measuring the cyclotron frequency for one ion at different detunings from the detector resonance frequency. Corrections were also made for the small shift in the average position between the two ions due the change in trap voltage, combined with the magnetic field gradient; and also for the polarizabilty of the H_2^+ ion [42, 43]. With an outer ion cyclotron radius of 2 mm, the effect of ion-ion interaction on the CFR was below 10^{-12} and so negligible [36]; the effect of image charges [44] was also negligible.

Results and Conclusions.– Combining the average of the results in Fig. 2 with the corrections in Table III we obtain our final corrected H_2^+/D^+ CFR, which is equal to the mass ratio of D^+ to H_2^+, with H_2^+ in its ro-vibrational groundstate,

$$M[D^+]/M[H_2^+(0,0)] = 0.999\ 231\ 660\ 004(7)(7)(16)(19),$$

where in parentheses we give the uncertainties due to statistics, instrumental systematics, rotational energy, and the total uncertainty, respectively. By correcting for the mass of the electron [2, 3] and the binding energy of $H_2^+(0,0)$ [26, 45] we obtain our result for m_d/m_p which is shown in Table IV. Also in Table IV are the result of taking the ratio of m_d from Zafonte and Van Dyck [19] and m_p from Heisse *et al.* [5]; the result from the H_2^+/D^+ measurement of Solders *et al.* [21]; and the value from the CODATA-18 adjustment [2]. As can be seen our m_d/m_p is smaller by nearly two standard deviations, and has an uncertainty a factor of two smaller than the ratio of m_d from [19] and m_p from [5]. Our result is in fair agreement with, but a factor of 9 more precise than the value from the previous measurement of the CFR of H_2^+ to D^+ [21]; and in agreement, but a factor of three more precise than the CODATA-18 value. Our m_d/m_p can be combined with the m_p of [5] to give m_d =2.013 553 212 586(76) u, which is 159(86) × 10^{-12} u less than the result of [19]. Such a value for m_d would reduce the current discrepancy in $m_d + m_p - m_h$ between the value obtained from the mass ratio of HD^+ to $^3He^+$ of [33], and that from using individual atomic mass measurements, see [5, 33], from 484(97) to 325(134) × 10^{-12} u, reducing but not removing the discrepancy. Hence, further atomic mass measurements of ^3He, as well as of the deuteron and proton are motivated. Combining our m_d/m_p with m_p of [5] and the binding energy of the neutron 0.002 388 169 95(42) u [18], gives a neutron atomic mass of 1.008 664 915 94(42) u, in good agreement with the CODATA-18 value [2].

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