

Rotational Energy as Mass in H_3^+ and Lower Limits on the Atomic Masses of D and ^3He

J. A. Smith, S. Hamzeloui, D. J. Fink, and E. G. Myers

Department of Physics, Florida State University, Tallahassee, Florida 32306-4350, USA



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We have made precise measurements of the cyclotron frequency ratios H_3^+/HD^+ and $\text{H}_3^+/^3\text{He}^+$ and observe that different H_3^+ ions result in different cyclotron frequency ratios. We interpret these differences as due to the molecular rotational energy of H_3^+ changing its inertial mass. We also confirm that certain high J , K rotational levels of H_3^+ have mean lifetimes exceeding several weeks. From measurements with the lightest H_3^+ ion we obtain lower limits on the atomic masses of deuterium and helium-3 with respect to the proton.

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Precision measurements of cyclotron frequencies of single ions in a cryogenic Penning trap yield atomic mass ratios with application to fundamental constants and tests of fundamental physics [1–3]. Changes in cyclotron frequency have also been used to detect the rotational state of molecular ions with body-frame dipole moments due to their large polarizability [4–7]. In this Letter, we show sensitivity to the rotational state of a molecular ion simply through the change in inertial mass, and hence cyclotron frequency, due to the extra internal energy [8]. This more general method for nondestructive state detection opens the possibility for repeated spectroscopic measurements on a single ion for many months, in contrast to sensitive methods that rely on ion counting after chemical reaction or photodissociation, e.g., see Refs. [9,10]. In particular, it may enable precision measurements on exotic species such as the antihydrogen molecular ion [11], with application to tests of fundamental symmetries.

In a recent paper [12], we described a precise measurement of the atomic mass ratio $M[^3\text{He}^+]/M[\text{HD}^+]$, which yielded the mass difference $m_p + m_d - m_h$, where m_p , m_d , and m_h are the atomic masses (relative to ^{12}C) of the proton, deuteron, and the helion (the nucleus of ^3He). This confirmed a discrepancy, at over 4 standard deviations, between a previous measurement of $M[^3\text{He}^+]/M[\text{HD}^+]$ [3] and the value for $m_p + m_d - m_h$ obtained from the most recent literature values for m_p [13–15], and m_d and m_h [16], obtained by direct measurements with respect to ions of ^{12}C . This discrepancy is sometimes referred to as the helium-3 puzzle [15], although it could also indicate underestimated uncertainties in the literature values for m_p and m_d . To provide additional confirmation of our result for $\text{HD}^+/^3\text{He}^+$, we also measured the cyclotron frequency ratios (CFRs) H_3^+/HD^+ and $\text{H}_3^+/^3\text{He}^+$. The ratio of these ratios provided additional values for $\text{HD}^+/^3\text{He}^+$. When, as reported in Ref. [12], both CFRs were measured with the same H_3^+ ion, the ratio of H_3^+/HD^+ to $\text{H}_3^+/^3\text{He}^+$ was in good agreement with the direct measurement of

$\text{HD}^+/^3\text{He}^+$. However, as we discuss here, CFRs measured with different H_3^+ ions gave different results.

This variation in CFRs involving H_3^+ , which was as large as 2×10^{-10} , nearly an order of magnitude greater than our resolution, can be understood as due to different amounts of internal energy of the H_3^+ changing its inertial mass. Because of its equilateral triangle structure, and hence no body-frame electric dipole moment, H_3^+ is known theoretically to have highly metastable rotational levels [17–20]. As has been shown by studies of dissociative recombination and Coulomb explosion imaging in a storage ring [21,22], such levels can be populated up to at least 1 eV when the H_3^+ is formed. On the other hand, these studies also show, consistent with theoretical predictions [18], that H_3^+ has no excited vibrational levels with mean lifetimes greater than a few seconds. Hence, we interpret the different CFRs as being due to different rotational energies of the H_3^+ . While, for several decades, single ion Penning trap techniques have required corrections to the mass of molecular ions due to electronic and vibrational energy [23–25], this is the first observation of mass due to rotational energy.

Our results also confirm theoretical predictions that, in the astrophysically important H_3^+ ion, certain high J , K rotational levels have mean lifetimes greater than several weeks [19]. (Here, J specifies the total angular momentum and K specifies the absolute value of its projection onto the symmetry axis.) In this they complement storage ring measurements which show H_3^+ ions remaining rotationally excited for more than 10 s [21], as well as astronomical observations, by infrared absorption spectroscopy [17], of large interstellar concentrations of H_3^+ in excited but lower J , K levels such as (3,3).

Another reason for measuring the H_3^+/HD^+ and $\text{H}_3^+/^3\text{He}^+$ CFRs is that they relate m_d and m_h separately to m_p . While this goal is partially frustrated by the additional mass of the H_3^+ , we can still use the CFR with the lightest H_3^+ to give upper bounds on the mass

differences $2m_p - m_d$ and $3m_p - m_h$. Of these, we find that the latter is significantly smaller than the same difference obtained using a value for m_p from Ref. [15], and for m_h from Ref. [16]. That is, our results indicate that the continuing 4σ discrepancy in $m_p + m_d - m_h$ reported in Ref. [12] is (at least) partly due to a higher mass for the helion relative to the proton than as obtained from Refs [15,16].

Method.—The H_3^+/HD^+ and $\text{H}_3^+/\text{}^3\text{He}^+$ CFRs were obtained by alternately and repeatedly measuring the cyclotron frequencies of each ion in a pair, the ions being simultaneously trapped in an 8.5-T precision Penning trap, whose vacuum enclosure is immersed in liquid helium at 4.2 K [1]. The cyclotron frequency of one ion, at the center of the trap, was measured using the pulse-and-phase technique [26], while the other ion was placed in a 2-mm-radius cyclotron orbit, after which the ions were interchanged. With a separation of 2 mm, ion-ion interaction had a negligible effect on the measured CFRs [12,27]. Each run lasted between 6 and 10 h and consisted of up to 2×22 interleaved cyclotron frequency measurements for the two ions, yielding a CFR with a statistical (1σ) uncertainty $(3\text{--}6) \times 10^{-11}$.

The HD^+ or $\text{}^3\text{He}^+$ ions were made inside the trap by electron beam ionization using a nominal 10-nA electron beam from a field emission point (FEP), with $\text{}^3\text{He}$ or HD injected as a pulsed molecular beam. In the case of H_3^+ , which we assume was produced by the $\text{H}_2 + \text{H}_2^+$ reaction [17], we operated the FEP for periods up to 30 s, without injecting any gas, the H_2 presumably being liberated from surfaces impacted by the electron beam. After unwanted ions were eliminated, the desired ion pair remained trapped for periods of days to months, limited only by collisions with residual gas molecules in the extreme vacuum. The results reported here were taken within a data-taking campaign that provided the $\text{}^3\text{He}^+/\text{HD}^+$ result reported in Ref. [12], and more experimental details can be found there.

Cyclotron frequency ratios.—Table I summarizes the average CFRs and corresponding mass differences between the ions. In the first column, (1) and (2) indicate the first

and second H_3^+ ions made, while (3a), (3b), and (3c) refer to the same third ion, but with measurements separated by 40 and 80 days, respectively. In the case of $\text{H}_3^+(2)$, after measuring the CFR with respect to $\text{}^3\text{He}^+$, the $\text{}^3\text{He}^+$ was removed and a HD^+ ion was then made within 0.2 mm of the axis of the trap, and so well inside the 2-mm-radius cyclotron orbit of $\text{H}_3^+(2)$. The sixth column gives the correction due to imbalance in the cyclotron radii (which results in different relativistic frequency shifts for the two ions), while the seventh gives the correction [5] due to the large polarizability of HD^+ in its rovibrational ground state [28,29], and the small polarizability of H_3^+ in its vibrational ground state [30,31]. The last column gives the atomic mass differences between the ions, $M[\text{H}_3^+] - M[\text{X}^+]$, where $\text{X}^+ = \text{HD}^+$ or $\text{}^3\text{He}^+$, along with the statistical uncertainty, and systematic uncertainty, which we take to be 100% of the imbalance correction. As discussed in Ref. [12], because the ions in our pairs are very similar in mass, all known systematic shifts to the CFRs are estimated to be $\ll 1 \times 10^{-11}$, with the exception of the shift due to imbalance in the cyclotron radii. This systematic is completely correlated with the ion pair type and does not affect the changes in a given ratio due to changes in the mass of the H_3^+ .

Variation of the mass of H_3^+ .—In Fig. 1, we show the mass differences $M[\text{H}_3^+] - M[\text{HD}^+]$ and $M[\text{H}_3^+] - M[\text{}^3\text{He}^+]$ from the last column of Table I. In the case of $\text{H}_3^+(2)/\text{}^3\text{He}^+$ and $\text{H}_3^+(2)/\text{HD}^+$, where data taking took place for 31 and 9 days, respectively, we have shown the averages of 6 smaller groups of runs, each lasting 4 days or fewer, that make up the 13 runs for each pair. No statistically significant variation in the mass difference for $\text{H}_3^+(2)$ is seen on this shorter timescale. Similarly, although not shown in the figure, there is no statistically significant variation between the three runs that are averaged to give point (3a). In Fig. 1 we have used different offsets of 0.001 548 279 000 and 0.007 445 752 161 u for $M[\text{H}_3^+] - M[\text{HD}^+]$ and $M[\text{H}_3^+] - M[\text{}^3\text{He}^+]$, respectively, which vertically aligns the two different mass differences for $\text{H}_3^+(2)$. This corresponds to assuming that the mass of

TABLE I. Average uncorrected cyclotron frequency ratios and resulting corrected mass differences for the different ion pairs. “Dates” indicates the date (in 2017) of the first and last run used to form the average, “Age” is the age in days of the H_3^+ ion at the start of data taking, “Runs” is the number of runs used in the average, R_{unc} is the uncorrected average CFR, with statistical uncertainty in parentheses, Δ_{imb} (in units of 10^{-12}) is the estimated correction for imbalance in the cyclotron radii, Δ_{pol} (in units of 10^{-12}) is the correction due to the polarizabilities of the HD^+ and H_3^+ ions. $M[\text{H}_3^+] - M[\text{X}^+]$ (with statistical and systematic uncertainties in parentheses) is the corrected ion mass difference obtained from the ratio.

Ion pair	Dates	Age	Runs	R_{unc}	Δ_{imb}	Δ_{pol}	$M[\text{H}_3^+] - M[\text{X}^+]$ (u)
$\text{H}_3^+(1)/\text{HD}^+$	2/6–2/12	40	5	0.999 487 821 168(19)	−5	−94	0.001 548 279 271(56)(14)
$\text{H}_3^+(2)/\text{}^3\text{He}^+$	3/9–4/9	3	13	0.997 536 905 750(10)	−26	1	0.007 445 753 007(29)(78)
$\text{H}_3^+(2)/\text{HD}^+$	4/13–4/21	38	13	0.999 487 820 978(11)	−4	−94	0.001 548 279 846(32)(14)
$\text{H}_3^+(3a)/\text{}^3\text{He}^+$	6/26–6/28	0.5	3	0.997 536 905 833(18)	−22	1	0.007 445 752 743(55)(65)
$\text{H}_3^+(3b)/\text{}^3\text{He}^+$	8/8–8/14	43	8	0.997 536 905 902(14)	−22	1	0.007 445 752 534(43)(65)
$\text{H}_3^+(3c)/\text{}^3\text{He}^+$	10/28–10/31	124	4	0.997 536 905 887(14)	−22	1	0.007 445 752 579(41)(65)

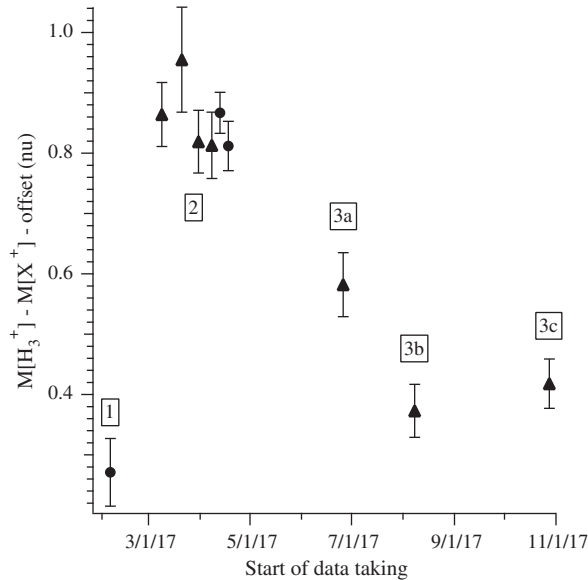


FIG. 1. Ion mass differences measured with the three H_3^+ ions. Data for $M[\text{H}_3^+] - M[\text{HD}^+]$ are indicated by round points, and for $M[\text{H}_3^+] - M[{}^3\text{He}^+]$ by triangles.

the H_3^+ ion remained constant throughout all the data taking for $\text{H}_3^+(2)$, and enables the data for all mass differences to be displayed on a single figure. This assumption is consistent with the good agreement between the ratio of the two CFRs $\text{H}_3^+(2)/{}^3\text{He}^+$ and $\text{H}_3^+(2)/\text{HD}^+$ and the direct measurement of the $\text{HD}^+/\text{}^3\text{He}^+$ CFR as reported in Ref. [12]. We also note, as reported in Ref. [12], that the two separate measurements made of the $\text{HD}^+/\text{}^3\text{He}^+$ CFR, using different HD^+ and ${}^3\text{He}^+$ ions, one starting on 2/16/17 and the other on 6/14/17, were in good agreement, giving $R_{\text{unc}} = 0.998\,048\,085\,049(13)$ and $0.998\,048\,085\,042(27)$, respectively, showing the reproducibility of our measurements at different times. Since HD^+ has a body-frame dipole moment, all its excited rotational and vibrational levels have relatively short lifetimes. Moreover, the first excited rotational state, which has mean lifetime of 149 s [32], is 1.3 THz above the ground state. Therefore, in the 4.2 K environment of our Penning trap, the HD^+ is expected to remain in its rovibrational ground state.

Hence, we interpret the variation in mass differences shown in Table I and Fig. 1 as being due to differences in the mass of the three different H_3^+ ions due to differences in internal energy. In particular, the data for H_3^+/HD^+ show that $\text{H}_3^+(2)$ had 0.54(6) eV more internal energy than $\text{H}_3^+(1)$, while the data for $\text{H}_3^+/\text{}^3\text{He}^+$ show (2) had 0.25(6) eV more energy than (3a). $\text{H}_3^+(3)$ then apparently lost 0.19(7) eV between 6/27/17 (3a) and 8/8/17 (3b), but did not change significantly, 0.04(6) eV, after a further 10 weeks (3c).

In Fig. 2, we show some of the rotational levels of the ground vibrational level of H_3^+ based on the theoretical results of Mizus *et al.* [19], specifically those with $J = K$

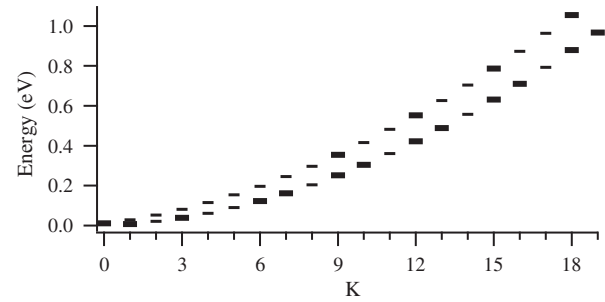


FIG. 2. Rotational levels of the ground vibrational level of H_3^+ with $J = K$ (lower) or $K + 1$ (upper), for $J \leq 19$. Levels that are absolutely stable against electric dipole decay are shown with heavier lines.

and $J = K + 1$. Because the parity is given by $(-1)^K$, electric-dipole ($E1$) transitions change K and are allowed only by centrifugal distortion [33,34]. Moreover, levels with $K = 3n$, with n integral, have ortho symmetry with total nuclear spin $I = 3/2$, while $K = 3n + 1$ and $K = 3n + 2$ are para with $I = 1/2$, and para to ortho transitions are strongly forbidden. This results in a number of rotational levels of H_3^+ that are highly metastable. In particular, most levels for K up to at least 19, where $J = K = 3n$ and $3n + 1$, and also where $J = K + 1$, with $K = 3n$, have no lower level to which an $E1$ transition is allowed. The exceptions are (4,4), (4,3), and (7,6). In Fig. 2, those levels absolutely stable against $E1$ decay are indicated by heavier lines. However, $E1$ transitions that satisfy the above selection rules are strongly attenuated unless they also satisfy $\Delta k = \pm 3$, where k is the signed quantum number corresponding to K . So, $J = K$ levels for $5 \leq K \leq 14$ with $K = 3n + 2$ and $J = K + 1$ levels for $7 \leq K \leq 14$ with $K = 3n + 1$ and $K = 3n + 2$ have mean lifetimes greater than 10^7 s, and so do the (4,4) and (7,6) levels [19,35]. On the other hand, since transitions with $\Delta J = 0, \pm 1$, $\Delta K = +3$ are relatively strong, relaxation into the highly metastable levels can be expected in timescales of hours or less, as has been modeled for storage ring data [36–38].

With the limited number of mass differences and limited resolution it is not possible to identify individual rotational levels. However, comparing Fig. 1 with Fig. 2 we see that the heaviest H_3^+ ion, that is (2), which was observed not to change mass for 43 days, was, at the 2σ level of uncertainty, in a level at least as high in energy as $(J, K) = (12, 12)$, while (3a), in June, was at least as high as (7,7). The loss of rotational energy between (3a) and (3b), while possibly due to radiative decay, could also be due to a collision with a neutral. In any case, our data for mass differences show rotational energy storage by H_3^+ for many weeks.

Lower limits on the mass of D and ${}^3\text{He}$ relative to the proton.—Although the unknown rotational energy prevents us from directly relating the mass of HD^+ or ${}^3\text{He}^+$ to H_3^+ in its ground level, we can still use our results to obtain upper limits for $2m_p - m_d$ and $3m_p - m_h$. Using theoretical

TABLE II. Mass difference upper limits obtained from our cyclotron frequency ratios compared with mass differences from the literature. For “This work” the numbers in parentheses are the statistical, systematic, and total uncertainty, and for “Refs. [15,16]” they are the respective contributions from Refs. [15,16], and the combined uncertainty.

Difference	Source	Result (u)
$2m_p - m_d$	This work	$<0.000\,999\,720\,564(56)(14)(58)$
	Refs. [15,16]	$0.000\,999\,720\,421(66)(40)(77)$
$3m_p - m_h$	This work	$<0.006\,897\,152\,754(68)(74)(100)$
	Refs. [15,16]	$0.006\,897\,153\,081(99)(43)(108)$

values for the energies of formation of the ions in their ground levels, and the mass of the electron [14,39], we can convert ion mass differences to mass differences between their nuclei without significant loss of precision. The ionization energy of ${}^3\text{He}^+$ is taken from Ref. [40], while the energy of formation of HD^+ in its ground state, with respect to separated e , p , and d , has been accurately calculated in Ref. [28]. The energy of formation of H_3^+ in its (1,1) ground level has been determined to be $-36.018\,90(2)$ eV with respect to $3p$ and $2e$. This was obtained by combining precise Born-Oppenheimer potential calculations [41] with the zero-point energy and the excitation energy of the (1,1) level with respect to the symmetry forbidden (0,0) level [42].

In Table II we show the upper limits for $2m_p - m_d$ and $3m_p - m_h$ from our measurements. In the first row we show the upper limit for $2m_p - m_d$ obtained directly from our H_3^+/HD^+ measurements in February with the lightest $\text{H}_3^+(1)$. In the second row we show the same mass difference obtained using m_p from Ref. [15] and m_d from Ref. [16]. In the third row we show the result obtained for $3m_p - m_h$ by combining the February H_3^+/HD^+ ratio with our measurement of the $\text{HD}^+/\text{}^3\text{He}^+$ ratio as reported in Ref. [12]; namely, $M[{}^3\text{He}^+]/M[\text{HD}^+] = 0.998\,048\,085\,122(12)(20)(23)$. In the fourth row we show the same mass differences as obtained using m_p from Ref. [15] and m_h given in Ref. [16]. We see that our upper limit for the $2m_p - m_d$ difference is consistent with the difference obtained from the direct measurements relative to ${}^{12}\text{C}$. However, our upper limit for the $3m_p - m_h$ shows a discrepancy of $0.33(15)$ nu.

Conclusions and further work.—We have carried out precise measurements of the cyclotron frequency ratios H_3^+/HD^+ and $\text{H}_3^+/\text{}^3\text{He}^+$. Measurements with different H_3^+ ions show differences that are consistent with the ions occupying rotationally excited levels up to at least 0.5 eV, and that such levels have lifetimes greater than several weeks. By identifying the lightest H_3^+ ions we are able to obtain upper limits on the mass differences $2m_p - m_d$ and $3m_p - m_h$. Of these, the former is consistent with the measurements relative to ${}^{12}\text{C}$ [15,16]. However, our upper limit for the $3m_p - m_h$

difference is smaller, by more than $0.33(15)$ nu, than the result from the individual measurements of m_p [15] and m_h [16] with respect to ${}^{12}\text{C}$. This indicates that the 4 standard deviation discrepancy for $m_p + m_d - m_h$ discussed in Ref. [12] is at least partly due to a heavier helion or lighter proton compared to Refs. [15,16]. More work will be required to fully resolve this discrepancy. Finally, we note that extensions of these techniques may enable the rotational state to be identified and lead to nondestructive spectroscopy and lifetime measurements on a single H_3^+ ion.

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