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# Rotational Energy as Mass in $\text{H}_3^+$ and Lower Limits on the Atomic Masses of D and $^3\text{He}$

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# Rotational energy as mass in $\text{H}_3^+$ and lower limits on the atomic masses of D and $^3\text{He}$

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

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 non-destructive 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 photo-dissociation *e.g.* see, [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  $^{12}\text{C}$ ) of the proton, deuteron and the helion (the nucleus of  $^3\text{He}$ ). 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  $^{12}\text{C}$ . 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)  $\text{H}_3^+/\text{HD}^+$  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 [12], both CFRs were measured with the same  $\text{H}_3^+$  ion, the ratio of  $\text{H}_3^+/\text{HD}^+$  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  $\text{H}_3^+$  ions gave different results.

This variation in CFRs involving  $\text{H}_3^+$ , which was as large as  $2 \times 10^{-10}$ , nearly an order of magnitude greater than our resolution, can be understood as due to different amounts of internal energy of the  $\text{H}_3^+$  changing its inertial mass. Because of its equilateral triangle structure, and hence no body-frame electric dipole moment,  $\text{H}_3^+$  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  $\text{H}_3^+$  is formed. On the other hand, these studies also show, consistent with theoretical predictions [18], that  $\text{H}_3^+$  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  $\text{H}_3^+$ . 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  $\text{H}_3^+$  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  $\text{H}_3^+$  ions remaining rotationally excited for more than 10 s [21]; as well as astronomical observations, by infra-red absorption spectroscopy [17], of large interstellar concentrations of  $\text{H}_3^+$  in excited but lower  $J, K$  levels such as (3,3).

Another reason for measuring the  $\text{H}_3^+/\text{HD}^+$  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  $\text{H}_3^+$ , we can still use the CFR with the lightest  $\text{H}_3^+$  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 [15], and for  $m_h$  from [16]. That is, our results indicate that the continuing 4-sigma discrepancy in  $m_p + m_d - m_h$  reported

in [12] is, (at least) partly due a higher mass for the helium relative to the proton, than as obtained from [15] and [16].

*Method:* The  $\text{H}_3^+/\text{HD}^+$  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 tesla 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 hours and consisted of up to  $2 \times 22$  interleaved cyclotron frequency measurements for the two ions, yielding a CFR with a statistical (one-sigma) uncertainty 3 to  $6 \times 10^{-11}$ .

The  $\text{HD}^+$  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  $\text{HD}$  injected as a pulsed molecular beam. In the case of  $\text{H}_3^+$ , which we assume was produced by the  $\text{H}_2 + \text{H}_2^+$  reaction [17], we operated the FEP for periods up to 30 seconds, without injecting any gas, the  $\text{H}_2$  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 [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  $\text{H}_3^+$  ions made, while 3a, 3b, 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 an  $\text{HD}^+$  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  $\text{HD}^+$  in its ro-vibrational ground state [28, 29], and the small polarizability of  $\text{H}_3^+$  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 [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  $\text{H}_3^+$ .

*Variation of the mass of  $\text{H}_3^+$ :* 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 less, 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 time scale. 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 u 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 the  $\text{H}_3^+$  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  $\text{H}_3^+(2)/\text{}^3\text{He}^+$  and  $\text{H}_3^+(2)/\text{HD}^+$ , and the direct measurement of the  $\text{HD}^+/\text{}^3\text{He}^+$  CFR as reported in [12]. We also note, as reported in [12], that the two separate measurements made of the  $\text{HD}^+/\text{}^3\text{He}^+$  CFR, using different  $\text{HD}^+$  and  $\text{}^3\text{He}^+$  ions, one starting on 2/16 and the other on 6/14, 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  $\text{HD}^+$  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 sec [32], is 1.3 THz above the groundstate. Therefore, in the 4.2 K environment of our Penning trap, the  $\text{HD}^+$  is expected to remain in its ro-vibrational groundstate.

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  $\text{H}_3^+$  ions due to differences in internal energy. In particular, the data for  $\text{H}_3^+/\text{HD}^+$  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 (3a) and 8/8 (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  $\text{H}_3^+$  based on the theoretical results of Mizus et al. [19], specifically those with  $J = K$  and  $J = K + 1$ . Because the parity is given by  $(-1)^K$ , electric-dipole (E1) transitions change  $K$  and are

TABLE I. Average uncorrected cyclotron frequency ratios and resulting corrected mass differences for the different ion pairs. “Dates” indicates the date of the first and last run used to form the average; “Age” is the age in days of the  $\text{H}_3^+$  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;  $\Delta_{imb}$  (in units of  $10^{-12}$ ) is the estimated correction for imbalance in the cyclotron radii;  $\Delta_{pol}$  (in units of  $10^{-12}$ ) is the correction due to the polarizabilities of the  $\text{HD}^+$  and  $\text{H}_3^+$  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	$R_{unc}$	$\Delta_{imb}$	$\Delta_{pol}$	$M[\text{H}_3^+] - M[\text{X}^+]$ (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)
$\text{H}_3^+(2)/^3\text{He}^+$	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)
$\text{H}_3^+(3a)/^3\text{He}^+$	6/26 - 6/28	0.5	3	0.997 536 905 833(18)	-22	1	0.007 445 752 743(55)(65)
$\text{H}_3^+(3b)/^3\text{He}^+$	8/8 - 8/14	43	8	0.997 536 905 902(14)	-22	1	0.007 445 752 534(43)(65)
$\text{H}_3^+(3c)/^3\text{He}^+$	10/28 - 10/31	124	4	0.997 536 905 887(14)	-22	1	0.007 445 752 579(41)(65)

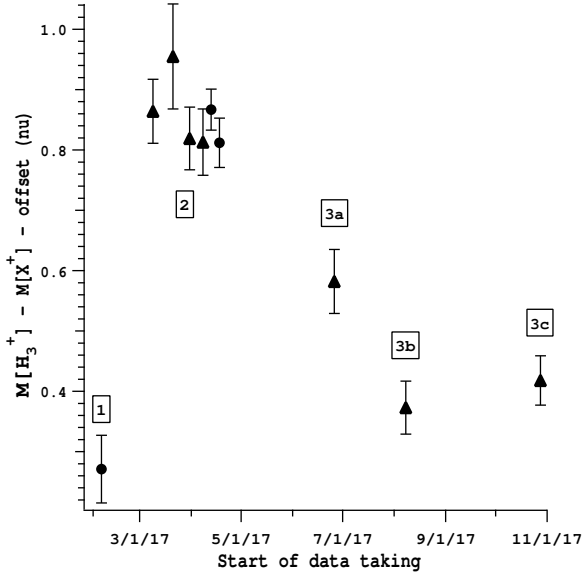


FIG. 1. Ion mass differences measured with the three  $\text{H}_3^+$  ions. Data for  $M[\text{H}_3^+] - M[\text{HD}^+]$  are indicated by round points, for  $M[\text{H}_3^+] - M[^3\text{He}^+]$  by triangles.

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  $\text{H}_3^+$  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

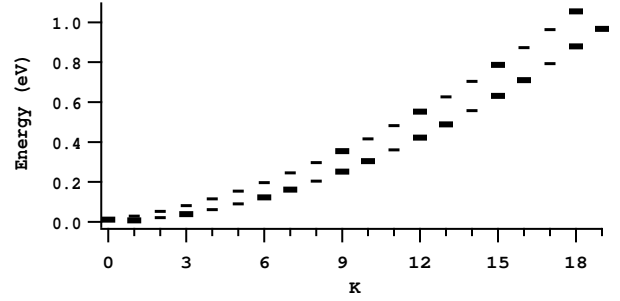


FIG. 2. Rotational levels of the ground vibrational level of  $\text{H}_3^+$  with  $J = K$  (lower) or  $K + 1$  (upper), for  $J \leq 19$ . Levels that are absolutely stable against electric dipole decay are shown with heavier lines.

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 time scales 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  $\text{H}_3^+$  ion, that is (2), which was observed not to change mass for 43 days, was, at the 2-sigma 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  $\text{H}_3^+$  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  $\text{HD}^+$  or  $^3\text{He}^+$  to  $\text{H}_3^+$  in its ground level, we can still use our results to obtain upper limits for  $2m_p - m_d$  and  $3m_p - m_h$ . Us-

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; for “Refs. [15, 16]” they are the respective contributions from [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]	$0.006\,897\,153\,081(99)(43)(108)$

ing theoretical 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 [40], while the energy of formation of  $\text{HD}^+$  in its ground state, with respect to separated  $e$ ,  $p$  and  $d$ , has been accurately calculated in [28]. The energy of formation of  $\text{H}_3^+$  in its (1,1) ground level has been determined to be  $-36.01890(2)$  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  $\text{H}_3^+/\text{HD}^+$  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 [15] and  $m_d$  from [16]. In the third row we show the result obtained for  $3m_p - m_h$  by combining the February  $\text{H}_3^+/\text{HD}^+$  ratio with our measurement of the  $\text{HD}^+/^3\text{He}^+$  ratio as

reported in [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 [15], and  $m_h$  given in [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  $\text{H}_3^+/\text{HD}^+$  and  $\text{H}_3^+/^3\text{He}^+$ . Measurements with different  $\text{H}_3^+$  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  $\text{H}_3^+$  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 [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 non-destructive spectroscopy and lifetime measurements on a single  $\text{H}_3^+$  ion.

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