

Penning-trap measurement of the atomic masses of ^{18}O and ^{19}F with uncertainties <0.1 parts per 10^9

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By confining pairs of ions in a Penning trap, and alternating each ion between large and small cyclotron orbits, we have measured the cyclotron frequency ratios $^{12}\text{CD}_3^+/^{18}\text{O}^+$, $^{12}\text{C}_2\text{D}_6^+/^{18}\text{O}_2^+$, $^{12}\text{C}_3^+/^{18}\text{O}_2^+$, $^{13}\text{CD}_3^+/^{19}\text{F}^+$, and $^{28}\text{SiH}_3^+/^{12}\text{C}^{19}\text{F}^+$. Combined with other measurements for H, D, ^{13}C , and ^{28}Si , these ratios yield the atomic masses $M(^{18}\text{O})=17.999\,159\,613\,0(13)$ u, and $M(^{19}\text{F})=18.998\,403\,162\,9(11)$ u, which improve on previous values in the Atomic Mass Evaluation (AME2003) by factors of 500 and 60, respectively. Our value for $M(^{18}\text{O})$ is lower than the AME2003 value by $1.4(7)$ μu .

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I. INTRODUCTION

In the last two decades the refinement of single-ion Penning trap mass spectrometry with image current detection has enabled mass measurements at 0.1 parts per billion (ppb) fractional precision or better of atoms ranging from ^1H to ^{136}Xe , e.g., see Refs. [1–17]. Here we report on sub 0.1-ppb Penning trap measurements of the atomic masses of ^{18}O and ^{19}F . These were obtained using a recently developed technique for measuring cyclotron frequency ratios of ion pairs in which both ions are simultaneously trapped in the same Penning trap, but with each ion being alternated between the trap center, where its cyclotron frequency is measured, and a large radius cyclotron “parking” orbit [13,16].

The atomic mass of ^{18}O as given in the 2003 Atomic Mass Evaluation (AME2003) [18] has an uncertainty of 0.7 μu (40 ppb), and was mainly determined from nuclear decay and reaction data linking it to the 0.01-ppb-precise Penning trap measurement of $M(^{16}\text{O})$, see Refs. [7,15]. The atomic mass of ^{19}F given in Ref. [18], with precision of 0.07 μu (4 ppb), was mainly determined from a measurement using an rf spectrometer [19]. For both atoms, new, cryogenic Penning trap measurements are appropriate additions to the table of the most precisely determined masses. For ^{18}O , an improved mass is required for the analysis of extensive, high-precision (approaching 1 ppb) rotational and rovibrational spectroscopy of six stable isotopic variants of the CO molecule (i.e., consisting of ^{12}C , ^{13}C , ^{16}O , ^{17}O , ^{18}O) [20,21]. By inputting precise masses an isotope-independent global fit can be obtained that includes parameters describing the breakdown of the Born-Oppenheimer approximation, similar to a recent analysis of rotational and rovibrational spectroscopic data for silicon sulfide (SiS) [22]. A preliminary analysis, using masses obtained from the AME2003, resulted in an inconsistency that could be resolved by adjusting the least-well known mass, that of ^{18}O , by approximately -1.3 μu . This is consistent with a measurement of the cyclotron frequency ratio $^{18}\text{OH}_3^+/^{21}\text{Ne}^+$ using a Penning trap with time-of-flight detection by Savard *et al.* [23], which yielded $M(^{18}\text{O})$ to a precision of 0.25 μu with a shift of -1.65 μu with respect to the AME2003. These results are confirmed by our more precise measurements. Further, using the existing mass of ^{16}O , and the mass of ^{18}O reported here, the fit to the spectroscopic data for CO can be used to obtain an improved

mass for ^{17}O , which is given in the AME2003 to 7 ppb. This will be reported elsewhere [20]. In the case of ^{19}F , our measurement agrees with the existing AME2003 value. However, the improved precision now allows ions obtained from gaseous fluorocarbons and hydrofluorocarbons to complement those from hydrocarbons, as a convenient series of precision references for mass spectrometers for heavy nuclear isotopes, analytical chemistry and other applications.

II. METHOD

Details of our apparatus and the method for measuring the cyclotron frequency can be found in Refs. [12,13] and only a summary is given here. We determine cyclotron frequencies of single ions confined at the center of a cryogenic Penning trap. The cyclotron frequency is defined as $f_c=qB/2\pi m$, where q and m are the charge and mass of the ion, and B (approximately 8.5 T) is the magnetic field at the position of the ion. We obtain f_c using the Brown-Gabrielse invariance theorem [24]: $f_c^2=f_{ct}^2+f_z^2+f_m^2$, in which f_{ct} , f_z , and f_m are the observable “trap-modified” cyclotron frequency, axial frequency, and magnetron frequency of the ion, respectively. Because of the hierarchy $f_m \ll f_z \ll f_{ct}$, only f_{ct} need be measured to the highest precision. This is done using the “pulse and phase” (PNP) technique [1,25]. A PNP consists of a short rf pulse which produces a dipole electric field which excites the cyclotron motion, here to a radius of 100 to 150 μm —followed by a variable delay of length T_{evol} in which the cyclotron motion evolves undetected and undamped—followed by a cyclotron-to-axial mode-coupling rf “pi-pulse,” which phase-coherently converts the cyclotron motion into axial motion, conserving the classical action [25]. We obtain the final phase of the cyclotron motion by fitting to the “ring-down” signal from the resulting axial motion, which also gives f_z . This signal is obtained from the image current induced by the ion’s axial motion in a resonant superconducting inductor, connected to the upper end-cap of the trap, and coupled to a dc SQUID. (This detection circuit, which has a Q of 33 000, requires that the trap voltage be adjusted for each ion, to keep f_z close to 213 kHz. Interaction between the ion and the detection circuit damps the axial motion; the on-resonance damping time being typically $\sim 1-2$ s.) The PNP procedure is repeated for a cycle of 10

TABLE I. Average cyclotron frequency (i.e., inverse mass) ratios and systematic corrections for each ion pair. N is the number of runs. Δ_{trap} , Δ_{i-i} , Δ_{f_z} , and Δ_{pol} are the systematic corrections in parts per trillion (ppt) with estimated uncertainty in parentheses, due to trap field imperfections, ion-ion interaction, shifts in f_z due to ion-detector interaction and differential voltage drift, and polarizability shifts (for CF^+), respectively. σ_{sys} is the total systematic error and σ_{stat} is the statistical error (in ppt) for each average ratio. $\langle R \rangle$ is the average ratio after applying systematic corrections, with statistical and systematic uncertainties combined in quadrature in parentheses.

Ion pair	N	Δ_{trap}	Δ_{i-i}	Δ_{f_z}	Δ_{pol}	σ_{sys}	σ_{stat}	$\langle R \rangle$
$^{12}\text{CD}_3^+ / ^{18}\text{O}^+$	7	-6(37)	-1(3)	-7(11)		39	30	0.997 608 564 116(50)
$^{12}\text{C}_2\text{D}_6^+ / ^{18}\text{O}_2^+$	7	3(51)	0(7)	7(13)		54	55	0.997 608 600 273(78)
$^{12}\text{C}_3^+ / ^{18}\text{O}_2^+$	3	0(16)	-4(51)	-9(12)		55	88	0.999 953 311 506(104)
$^{13}\text{CD}_3^+ / ^{19}\text{F}^+$	5	-1(26)	0(17)	5(10)		32	35	0.997 518 681 645(48)
$^{28}\text{SiH}_3^+ / ^{12}\text{C}^{19}\text{F}^+$	6	-1(17)	9(38)	0(10)	-80(40)	59	42	0.999 935 533 127(72)

different T_{evol} 's from 0.2 to 60 s. A single measurement of the trap-modified cyclotron frequency is hence obtained from $f_{ct} = (1/2\pi)d\phi/dT_{\text{evol}}$. For each T_{evol} the number of additional 2π 's to be added to the measured phase is determined by successively improved approximation of f_{ct} in moving from short to long T_{evol} 's. The value of f_z to associate with f_{ct} is the average from the 10 PNPs. f_m is obtained from $f_m = (f_z^2/2f_{ct})[1 + (9/4)\sin^2\theta_{\text{mag}}]$, where θ_{mag} is used to parametrize the effects of both trap tilt and ellipticity [24]. θ_{mag} is determined via a separate measurement of f_m using the ‘‘avoided-crossing method’’ [25].

A single measurement of f_c typically takes 5–10 min and has statistical precision of $\sim 3 \times 10^{-10}$, mainly limited by variations in the magnetic field of order 10^{-9} /h. To average out variations due to the magnetic field it is necessary to alternate between f_c measurements of each ion as quickly as possible. Here this is done using the technique described in Refs. [13,16]. The two ions to be compared are created in the Penning trap sequentially, other ions are eliminated, and the pair then remains simultaneously trapped, sometimes for over a week. (The unwanted ions are eliminated by exciting their axial motions while ensuring the axial motions of the desired ions are damped. The potential on the lower end cap is then reduced until the unwanted ions strike it.) The above PNP procedure is carried out on the ion at the center of the trap, while the other ion is ‘‘parked’’ in a cyclotron orbit, of radius, ρ_{ck} , up to 2 mm [26]. The ions are then interchanged by first partially reducing the cyclotron radius of the outer ion using a sequence of cyclotron-to-axial rf coupling pulses, with delays to allow the resulting axial motion to damp. The inner ion is then excited to ρ_{ck} using a single cyclotron drive pulse. The former outer ion is then cooled all the way to the trap center using a further sequence of cyclotron-to-axial coupling pulses. The new inner ion's cyclotron frequency is then measured using the PNP technique, and so on.

This swapping procedure takes from 5 to 15 min. This time increases rapidly with ρ_{ck} due to anharmonic shifts to the axial frequency that cause the coupling drive to be out of resonance. The swapping time and PNP cycle time together determine the number of interchanges that can be obtained in a run of typically 12 h duration, limited by the need to refill a liquid nitrogen dewar in our cryostat. This alternating-cyclotron-orbit method was initially developed using ions

with $m/q \approx 30$ [13]. With careful investigation of systematics it has produced mass ratio measurements with fractional precisions of 3×10^{-11} [16].

III. CYCLOTRON FREQUENCY RATIO MEASUREMENTS

The measurements presented here are of cyclotron frequency ratios of singly charged ions of the same total mass number which results in a large suppression of most systematic errors. Because of the higher cyclotron frequencies, the ratios $^{18}\text{O}^+ / ^{12}\text{CD}_3^+$ and $^{19}\text{F}^+ / ^{13}\text{CD}_3^+$ are expected to give the highest precision. However, since measurements at a different m/q , and with different differences in m/q between the ions in a pair, provide a control against systematic errors, we also measured the ratios $^{18}\text{O}_2^+ / ^{12}\text{C}_2\text{D}_6^+$, $^{18}\text{O}_2^+ / ^{12}\text{C}_3^+$, and $^{12}\text{C}^{19}\text{F}^+ / ^{28}\text{SiH}_3^+$.

In addition to ^{12}C , with atomic mass 12 u by definition, our reference ions include atoms whose masses are already known to high precision (0.1 ppb for H [6,18], 0.07 ppb for D [15], and 0.02 ppb for ^{13}C [9,10,16] and ^{28}Si [16]). The reference ions $^{12}\text{CD}_3^+$, $^{13}\text{CD}_3^+$, and $^{28}\text{SiH}_3^+$ have planar-equilateral-triangular structures in their electronic ground states. Hence, these ions should have no body-frame dipole moment, and hence no ‘‘orientation polarizability’’ that can produce a significant shift in the cyclotron frequency [10,16,27]. $^{12}\text{C}^{19}\text{F}^+$ does have a dipole moment, which has been calculated using multireference configuration interaction techniques to be 1.04 Debye [28]. Following Ref. [27], and allowing for the Boltzmann distribution of rotational state occupation probabilities, we estimate the average shift to the cyclotron frequency of the $^{12}\text{C}^{19}\text{F}^+$ ions during our measurements to be $-80(40)$ ppt.

Experimental [29] and theoretical [30–32] results imply that the ground electronic state of C_3^+ has a near-equilateral triangle geometry with a small dipole moment of order 0.1 a.u. or less. Theoretical studies [33–35] indicate that the lowest energy isomer of C_2D_6^+ has a C_{2h} point-group symmetry implying no dipole moment. Hence for these ions, the polarizabilities are expected to be negligible.

The results of our cyclotron frequency ratio measurements are given in Table I. Each ratio is the weighted average of between 3 and 7 data runs, each typically lasting 12 h. Systematic corrections and additional uncertainties are ap-

plied to allow for: magnetic and electrostatic field imperfections in the Penning trap; Coulomb interaction between the two ions; axial frequency shifts due to interaction of the ion with the detection circuit, and due to differential trap voltage drift; and, for the ratio involving $^{12}\text{C}^{19}\text{F}^+$, shifts due to the polarizability of the ion. Shifts to f_{ct} and f_z due to imperfections in the electrostatic and magnetic fields of our Penning trap are described in Ref. [12]. These shifts, which scale with even powers of the axial amplitude a_{zi} and the cyclotron radius ρ_{ci} of the inner ion, cancel in the cyclotron frequency ratio if a_{zi} and ρ_{ci} are balanced for the two ions. Small imbalances in a_{zi} and ρ_{ci} arise due to small detunings between the respective rf drive and motional frequencies of the ions. We estimate these imbalances, and using values for the lowest electrostatic field imperfections C_4 , which we null to $\sim 10^{-5}$ and $C_6=3(2)\times 10^{-3}$, and the main magnetic field imperfection $B_2/B_0=-5(3)\times 10^{-9}\text{mm}^{-2}$ [24], we obtain systematic corrections to apply to the average ratios. These are listed in Table I as Δ_{trap} . In estimating errors due to trap field imperfections, i.e., the error of Δ_{trap} , we also allow for the following larger effects: (a) possible small differences in C_4 between the ions due to errors in setting the guard-ring voltages and (b) conservatively, any difference in the observed axial amplitudes produced by the PNPs between the two ions, as obtained by analyzing the recorded amplitudes of the ring-downs. We note that, in comparison to Ref. [16], the systematic uncertainties that we have assigned are significantly larger. This is because the measurements of ^{18}O , ^{19}F reported here were the first to be made after, for unrelated reasons, we had cycled the cryogenic-UHV insert containing the Penning trap to room temperature and atmospheric pressure. This resulted in a shift and subsequent temporal variation, which required several months to stabilize, of the guard ring voltage required to cancel C_4 , and also resulted in an increase in C_6 by $\sim \times 3$ compared to the previous measurements. We also note, because all the ratios were measured with mass doublets, “equilibrium position shifts” [12], i.e., shifts to a ratio due to differences in the equilibrium positions of the two ions, combined with a linear magnetic gradient, are estimated to be negligible.

Perturbations due to the Coulomb interaction between the ions can be separated into “static” and “dynamical” effects [13]. Static effects are accounted for by modeling the outer ion as a thin ring of charge of radius ρ_{ck} that modifies the electrostatic potential experienced by the ion at the center of the trap. In analogy to the electrostatic field imperfections due to the trap electrodes, one can express the resulting shifts to f_z and f_{ct} of the inner ion as a series with terms proportional to $(\rho_{ci}/\rho_{ck})^{2n}\rho_{ck}^{-3}$ and $(a_{zi}/\rho_{ck})^{2n}\rho_{ck}^{-3}$, with $n=0, 1, 2$, etc. (the magnetron radius of the inner ion is reduced to $\ll \rho_{ci}$, so can be neglected). The $n=0$ terms, i.e., those independent of a_{zi} and ρ_{ci} , are equivalent to a change in trap voltage and produce shifts to f_z and f_{ct} that cancel when the invariance theorem is used to obtain f_c . Further, if a_{zi} , ρ_{ci} , and ρ_{ck} for the two ions are balanced between interchanges, these shifts cancel in the cyclotron frequency ratio. However, we estimate the possible imbalances in these amplitudes and calculate appropriate corrections to apply to the ratios.

The main dynamical effects result from the axial (and cyclotron) motion of the inner ion nonresonantly driving the

axial (cyclotron) motion of the outer ion. The outer ion then back-acts on the inner ion, resonantly driving the inner ion’s axial (cyclotron) motion, hence producing a frequency shift. These second-order shifts to the motional frequencies depend on the difference between the axial (and cyclotron) frequencies of the inner and outer ions and are analogous to the repulsive second order shifts between energy levels in quantum mechanics. The resulting shifts to the measured f_c ’s of the inner ion are in opposite directions for the two ions and so cause the measured cyclotron frequency ratio to be shifted. The sign of the shifts is such as to increase the absolute difference between the ratio and unity. However, since these shifts are expected to fall off as ρ_{ck}^{-6} , provided ρ_{ck} is sufficiently large, they are only a concern for ion pairs that are very close in m/q . Unfortunately, for $^{12}\text{C}_3^+/^{18}\text{O}_2^+$ and $^{28}\text{SiH}_3^+/^{12}\text{C}^{19}\text{F}^+$, with fractional mass differences $\sim 5\times 10^{-5}$, second-order shifts to the axial frequency f_z of the inner ion are significant for some of the values of ρ_{ck} used in this experiment. Further, estimating the resulting shift to the ratio is made complicated because the trap’s electrostatic field imperfections produce shifts to the outer ion’s f_z that vary as $\sim C_6\rho_{ck}^4$. This changes the difference between the f_z ’s of the inner and outer ion on which the shift depends. In particular, for a positive C_6 , when the heavy ion is in the large cyclotron orbit, its f_z is shifted closer to that of the inner ion, causing the second-order shift to increase. Hence estimating the resulting shift is limited by our uncertainty in C_6 as well as in ρ_{ck} . For all the ion pairs here, the second-order shift to the modified cyclotron frequency f_{ct} of the inner ion is negligible for $\rho_{ck}\geq 0.5$ mm.

As a general control against shifts to the cyclotron frequency ratio due to Coulomb interaction between the ions we took data with a range of parking radii. For $^{28}\text{SiH}_3^+/^{12}\text{C}^{19}\text{F}^+$ we looked for, and observed, a systematic shift to the ratio with $\rho_{ck}\leq 1.0$ mm: the average ratio $f_c(^{28}\text{SiH}_3^+)/f_c(^{12}\text{C}^{19}\text{F}^+)$ of two runs taken with $\rho_{ck}=0.9$ and 1.0 mm was shifted by $-2.1(9)\times 10^{-10}$ with respect to the average of 6 runs taken with $\rho_{ck}=1.5-1.75$ mm. For all the other ratios we observed no systematic variation in the ratio as a function of ρ_{ck} . Nevertheless, for all ion pairs, the final average ratios given in Table I include only runs for which $\rho_{ck}\geq 1.5$ mm. Our estimates of both the static and dynamical ion-ion interaction effects, with uncertainties, are included in Table I under Δ_{i-i} .

Finally, small shifts to the measured ratios arise due to the interaction of the axial motion of the centered ion and the resonance of the detector circuit. This results in a “pushing” of f_z by an amount that depends on its detuning from the detector resonance frequency. By measuring the detector and ion frequencies during the run we were able to correct for this effect. We also allowed for a small differential shift in our measurement of the axial frequencies of the two ions due to a differential drift in trap voltages: In our PNP technique the time corresponding to the measurement of f_{ct} is not exactly the same as the average time of the measurement of f_z . Hence, a drift in trap voltage that is different for the two ions can lead to a differential shift in the correct f_z to use in the invariance theorem. This effect is enhanced when rapidly switching between the two ions. The combined effect on the ratios of both these shifts to the axial frequency are listed under Δ_{f_z} in Table I.

TABLE II. Mass difference equations corresponding to the ratios given in Table I. The statistical, systematic, and total errors are shown in parentheses.

Ion pair	Mass difference	Result (u)
$^{12}\text{CD}_3^+ / ^{18}\text{O}^+$	$^{12}\text{C}+3(\text{D})-^{18}\text{O}$	0.043 145 722 16(54)(69)(88)
$^{12}\text{C}_2\text{D}_6^+ / ^{18}\text{O}_2^+$	$^{12}\text{C}+3(\text{D})-^{18}\text{O}$	0.043 145 721 16(98)(95)(136)
$^{12}\text{C}_3^+ / ^{18}\text{O}_2^+$	$3(^{12}\text{C})-2(^{18}\text{O})$	0.001 680 769 5(32)(20)(38)
$^{13}\text{CD}_3^+ / ^{19}\text{F}^+$	$^{13}\text{C}+3(\text{D})-^{19}\text{F}$	0.047 257 006 69(66)(62)(91)
$^{28}\text{SiH}_3^+ / ^{12}\text{C}^{19}\text{F}^+$	$^{28}\text{Si}+3\text{H}-^{12}\text{C}-^{19}\text{F}$	0.001 998 468 7(13)(18)(22)

IV. MASS DIFFERENCE EQUATIONS AND ATOMIC MASSES OF ^{18}O , ^{19}F

The cyclotron frequency ratios in Table I can be converted, without significant loss of precision, into linear equations that give mass differences between neutral atoms. To do this we account for the mass of the missing electrons and the electronic and chemical binding energies. The results are presented in Table II. In estimating the molecular binding energies we make use of “heats of formation at 0 K” [36,37] which apply to molecular ions in their ground vibrational states. This is appropriate for the heteronuclear diatomic ion CF^+ and for the polyatomic ions, since these do not have excited vibrational levels with lifetimes comparable to our ion trapping times of several hours or days. The exception is the homonuclear diatomic ion $^{18}\text{O}_2^+$, for which decay of vibrational excitation by electric dipole radiation is forbidden. However, assuming a mean vibrational quantum number following electron ionization of O_2 of $\langle v \rangle = 1.8$ [38], the maximum fractional shift to the cyclotron frequency is -1.2×10^{-11} , which we neglect.

Using the mass difference equations given in Table II and $M(\text{H}) = 1.007\,825\,032\,07(10)\text{u}$ [6,18], $M(\text{D}) = 2.014\,101\,778\,16(14)\text{u}$ [15], $M(^{13}\text{C}) = 13.003\,354\,835\,25(27)\text{u}$ [9,10,16], and $M(^{28}\text{Si}) = 27.976\,926\,534\,96(62)\text{u}$ [16], we obtain three values for $M(^{18}\text{O})$ and two for $M(^{19}\text{F})$. In Table III, these results, and their weighted averages, are compared to previous values in the AME2003 [18] and Ref. [23].

TABLE III. Atomic masses for ^{18}O and ^{19}F obtained from the different ratios, and their weighted averages, compared with previous values.

Atom	Source	Atomic mass (u)
^{18}O	$^{12}\text{CD}_3^+ / ^{18}\text{O}^+$	17.999 159 612 3(10)
	$^{12}\text{C}_2\text{D}_6^+ / ^{18}\text{O}_2^+$	17.999 159 613 3(15)
	$^{12}\text{C}_3^+ / ^{18}\text{O}_2^+$	17.999 159 615 3(20)
	Final average	17.999 159 613 0(13)
	AME2003 [18]	17.999 161 0(7)
	Savard <i>et al.</i> [23]	17.999 159 35(25)
^{19}F	$^{13}\text{CD}_3^+ / ^{19}\text{F}^+$	18.998 403 163 0(11)
	$^{28}\text{SiH}_3^+ / ^{12}\text{C}^{19}\text{F}^+$	18.998 403 162 5(23)
	Final average	18.998 403 162 9(11)
	AME2003 [18]	18.998 403 22(7)

Our values for the mass of ^{18}O obtained from $^{12}\text{CD}_3^+ / ^{18}\text{O}^+$ and $^{12}\text{C}_2\text{D}_6^+ / ^{18}\text{O}_2^+$ are in good agreement. These relate the same atomic masses but were obtained at different values of m/q . However, the mass of ^{18}O obtained from the ratio $^{12}\text{C}_3^+ / ^{18}\text{O}_2^+$ is higher than the average of the other two values by the fraction $1.4(1.2) \times 10^{-10}$. For our final value for the mass of ^{18}O , we used the weighted average of the three results given in Table III [with linear propagation of the systematic errors and error in $M(\text{D})$]. The $^{12}\text{C}_3^+ / ^{18}\text{O}_2^+$ data contributes only a 15% weight to this average value. This is because of the large systematic uncertainty for this ratio, due to the second-order dynamical shift to the axial frequency, and the large statistical uncertainty. For this ion pair there were only three measurements, due to the fact that it was difficult to make and isolate the $\sim 2\%$ fragment $^{12}\text{C}_3^+$ from the parent gas C_3H_4 . Nevertheless, we increased the uncertainty of our final result to $1.3 \mu\text{u}$ so that the value obtained from the $^{12}\text{C}_3^+ / ^{18}\text{O}_2^+$ result agrees at the 1σ level with our final result.

Our two results for the $M(^{19}\text{F})$ at different m/q are in good agreement. The mass obtained from $^{28}\text{SiH}_3^+ / ^{12}\text{C}^{19}\text{F}^+$ is less precise due to the additional mass of ^{12}C , and because the uncertainty in the ratio is increased due to second-order axial frequency shifts and the polarizability shift of $^{12}\text{C}^{19}\text{F}^+$. Again, for our final value, we took the weighted average of these two results.

V. CONCLUSIONS

By simultaneously trapping two ions in a Penning trap and comparing their cyclotron frequencies we have measured the atomic masses of ^{18}O and ^{19}F with estimated fractional uncertainties of less than 0.08 and 0.06 ppb, respectively. Our final result for $M(^{18}\text{O})$ is 17.999 159 613 0(13)u. This new value is $1.4(7)\mu\text{u}$ lower than the value in the AME2003 [18]. It agrees with the Penning trap result of Savard *et al.* [23] but improves the precision by nearly a factor of 200. It is more than sufficiently precise for use in global fits to recent molecular spectroscopy data of isotopomers of CO. For $M(^{19}\text{F})$ our final value is 18.998 403 162 9(11)u. This is in good agreement with the value given in the AME2003, mainly determined using an rf spectrometer [19], and is a factor of 60 more precise.

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