Mass Spectrometry at 0.1 Part Per Billion for Fundamental Metrology

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***Abstract*— The single ion Penning trap mass spectrometer at M.I.T. now compares masses with an accuracy of 0.1 part per billion. We have created a table of fundamental atomic masses and made measurements useful for calibrating the X-ray wavelength standard, and determining Avogadro's number, the molar Planck constant, and the fine structure constant.**

I. INTRODUCTION

THE long observation time and well understood dynamics of a single charged particle in a Penning trap have recently resulted in more than an order of magnitude improvement in the accuracy of mass spectrometry. Relative accuracies better than 10^{-10} have been reported [1]. In addition to improving traditional applications of mass spectrometry by one or two orders of magnitude, this higher precision is finding new applications in chemistry and physics including improved values of Avogadro's number, the fine structure constant, the neutrino mass, and (in the future) the weights of chemical bonds.

Several important advances in precision mass spectrometry have recently been made at the Massachusetts Institute of Technology. We have developed a new technique for precisely comparing the masses of ions with widely differing atomic weights that has allowed us to produce a table of 10 atomic masses which are of particular importance for metrology or for the determination of fundamental constants, including the mass of ^{28}Si which may allow replacement of the "artifact" mass standard with a silicon crystal [2]. We have also done a series of mass comparisons which effectively weigh γ-rays which, along with wavelength measurements of the same γ-rays, will allow calibration of the X-ray wavelength standard, as well as determination of the molar Planck constant $N_A h$ and the fine structure constant [3]. Finally we are laying the groundwork for substantially improving our precision by the squeezing of thermal noise, and by simultaneous measurement of two ions.

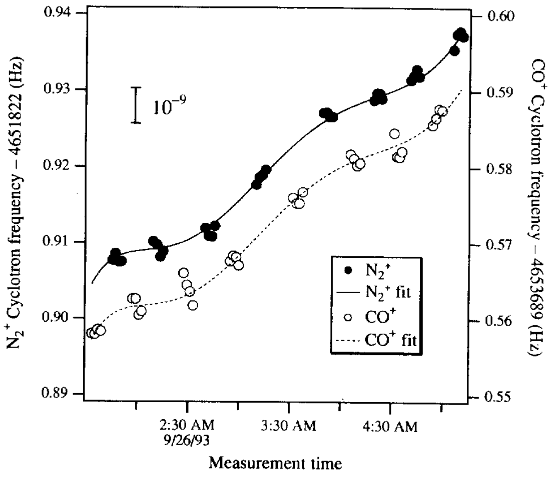

Fig. 1. Measurement of mass ratio of CO and N_2. Lines show a fit to the magnetic field drift.

II. MASS MEASUREMENTS

Our experimental approach is to measure the cyclotron frequencies of single molecular or atomic ions in a Penning trap, a highly uniform magnetic field with confinement along the (axial) direction of the field provided by weaker electric fields. Several unique features of our system enhance its accuracy. Axial oscillations are detected by a superconducting resonant circuit and a SQUID amplifier, permitting very low (160 kHz) axial frequencies and therefore very small electrostatic perturbations to the cyclotron frequency. The cyclotron frequency is measured by first exciting the cyclotron motion, then waiting for a specified time, and finally measuring the cyclotron phase by using a π-pulse to swap the axial and cyclotron modes. This technique has the advantage that, during the time of measurement (prior to the π-pulse), the cyclotron motion is unperturbed by drives or coupling [4]. Cyclotron frequencies of two ion species are measured repeatedly, alternating between the two ions. (See Fig. 1). A final value for the ratio is found by fitting the data to a low order polynomial that models the magnetic field drift. Our automated ion making process allows 20 or more ions to be loaded in a single night, resulting in overall uncertainty as small as 8×10^{-11}. Comparisons of non-doublets (ions with different mass numbers) are done using the same trap voltages for both measurements so that both ions will be located in precisely the same place [5]. Nondoublet measurements represent a significant advance in precision mass spectrometry since they allow direct comparison of any ion to ^{12}C, which weighs exactly 12 μ by definition. Table I lists our values for

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TABLE I
ATOMIC MASS TABLE. CENTER COLUMN SHOWS VALUES MEASURED AT M.I.T. LEFT COLUMN IS PREVIOUSLY ACCEPTED VALUES MEASURED BY CONVENTIONAL MASS SPECTROMETRY [6]

Atom	Mass (u)	Previous
^{1}H	1.007 825 031 6 (5)	... 035 0 (120)
n	1.008 664 923 5 (23)	... 919 0 (140)
^{2}H	2.014 101 777 9 (5)	... 779 0 (240)
^{13}C	13.003 354 838 1 (10)	... 826 0 (170)
^{14}N	14.003 074 004 0 (12)	... 002 0 (260)
^{15}N	15.000 108 897 7 (11)	... 970 0 (400)
^{16}O	15.994 914 619 5 (21)	... 630 0 (500)
^{20}Ne	19.992 440 175 4 (23)	... 600 0 (22000)
^{28}Si	27.976 926 532 4 (20)	... 100 0 (7000)
^{40}Ar	39.962 383 122 0 (33)	... 700 0 (14000)

TABLE II
CONSISTENCY CHECKS, SHOWING NUMBER OF DEGREES OF FREEDOM REDUCED CHI-SQUARE VALUES, AND THE PROBABILITY OF CHI-SQUARE EXCEEDING THE MEASURED VALUE

Check	v	χ_v^2	*P*
Repeated measurements	13	0.75	71%
Closed loops	3	1.53	20%
Redundant ratios	4	0.39	82%
Doublet / non-doublet	3	0.16	92%
Overall	24	0.74	81%

atomic masses [1] along with the previous values determined by conventional mass spectrometry [6]. Our values are one to three orders of magnitude more precise.

III. Consistency Checks

Numerous checks were made for systematic errors. The results of these checks are shown in Table II. Repeated measurements of the same ratios were made using slightly different magnetic or electric fields. We made several closed loops of measurements, which have the form, A/B, B/C, and C/A, the product of which must equal one. Related ratios, such as CH_4^+/O^+ and $C_2H_4^+/CO^+$, both of which determine the same mass difference, C + 4H − O, provide checks involving different trap voltages, different cyclotron frequencies, and different measured ratios. Several masses were determined by both doublet and non-doublet measurements (e.g. $^{40}Ar^{++}/^{20}Ne^+$ and $^{40}Ar^+/^{20}Ne^+$). Every mass in the table was determined from at least two independent sets of measurements. A fit of all 33 of the measured ratios to the values in Table I gives a χ^2 of 0.74. The consistency of all these results gives us confidence that our errors do not exceed the reported uncertainties.

IV. Fundamental Constants

Precise atomic masses make important contributions to metrology. Measurement of the lattice spacing of an isotopically pure crystal of ^{28}Si along with the atomic mass of silicon may soon allow measurement of Avogadro's number to a part in 10^8. At this accuracy, it would become practical to redefine the kilogram as a fixed number of atomic mass units, replacing the artifact standard kilogram [2]. There are also several fundamental constants that can be evaluated by weighing γ-rays. The molar Planck constant can be determined from the energy equation,

$$\Delta M c^2 = \frac{10^3 N_A hc}{\lambda} \tag{1}$$

where ΔM is the mass in u of a γ-ray whose wavelength is λ. The fine structure constant can then be found from $N_A h$ through the relation,

$$\alpha^2 = \frac{2R_\infty}{cM_p}\left\{\frac{M_p}{M_e}\right\}10^3 N_A h \tag{2}$$

where R_∞ is the Rydberg constant and M_p and M_e are the proton and electron atomic masses. Finally, the accurate determination of the atomic masses of γ-rays has contributed to a recalibration of γ- and X-ray standards. We have measured the difference between the masses of the neutron capture gamma rays of ^{14}N and H by determining the mass difference, $(^{15}N - ^{14}N) - (D - H) = -0.0092418527(9)\ \mu$. Similarly, for carbon we have $(^{13}C - ^{12}C) - (D - H) = -0.0029219082(11)$. Both of these numbers [1] represent roughly an order of magnitude improvement over previous measurements. Molecular ions are particularly well suited for these measurements. For example, the value for carbon can be determined directly from the mass ratio $^{13}CH_4^+/^{12}CDH_3^+$.

V. Conclusions and Progress Toward Higher Precision

Atomic mass comparisons can now be made within 0.1 part per billion or less. The principal limitations to our present accuracy are the tiny fluctuations in the magnetic field and uncertainty of the relativistic corrections due to thermal variations of the cyclotron amplitude. We are developing a technique for putting two different ions in the trap at the same time thereby eliminating the effect of field fluctuations [7], and we have demonstrated one technique [8] and theoretically examined several others for squeezing the thermal noise distribution to reduce amplitude uncertainties [9].

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