

Single-Ion Cyclotron Resonance Measurement of $M(\text{CO}^+)/M(\text{N}_2^+)$

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(Received 21 August 1989)

We have trapped single molecular ions in a precision Penning trap and, using cyclotron resonance techniques, have measured the mass ratio $M(\text{CO}^+)/M(\text{N}_2^+)$ to be 0.999 598 8876(4). Accuracy is limited at 4×10^{-10} predominantly by temporal instability in the magnetic field. All other systematic sources of error are $\Delta M/M \lesssim 10^{-10}$.

PACS numbers: 35.10.Bg, 07.75.+h

The Penning trap, with its strong uniform magnetic field and its much weaker electric field, has been used to perform a number of very accurate quantitative experiments.¹⁻⁴ We have used a Penning trap for mass spectroscopy using single-ion cyclotron resonance (SICR). The absence of ion-ion interaction makes systematics easy to understand; hence SICR is the most accurate method of comparing mass. The $\Delta M/M = 4 \times 10^{-10}$ result reported here, limited predominantly by the temporal drift in the magnetic field, is a factor of 6 better than the value from current tables,⁵ and may be the most accurate ion mass comparison to date.

A hyperbolic Penning trap⁶ consists of three main electrodes, all hyperbolic surfaces of rotation, which provide a restoring electric field which is linear with displacement along the axis of rotation. The much stronger axial magnetic field confines the particle radially. For a single charged particle there are three normal modes, one (the "axial" mode) that is aligned with the magnetic field, and two perpendicular to it. The perpendicular ("radial") modes are the electric field-modified cyclotron motion at frequency ν_c' and the slower magnetron orbit, due basically to $\mathbf{E} \times \mathbf{B}$ drift.

The ratio of the cyclotron frequencies for two different ion species, when corrected for electric field effects, is simply the inverse of their mass ratio. Our approach, then, is to compare the cyclotron frequencies of alternately loaded single ions. For an $M = 28$ amu ion, the cyclotron, axial, and magnetron frequencies in our trap are, respectively, $\nu_c' \cong 4.5$ MHz, $\nu_z \cong 160$ kHz, and $\nu_m \cong 2.8$ kHz.

Our trap hangs vertically in the bore of an 8.5-T superconducting Oxford magnet. The magnet has superconducting shims and a custom Dewar in the bore which allows us to cycle the trap from room temperature to 4.2 K while keeping the magnet itself cold. The main electrodes are precision-machined oxygen-free high-conductivity copper, plated with gold and coated with a layer of graphite particles (Aquadag) to minimize surface patch effects. The three main electrodes are spaced by machinable ceramic (MACOR) rings on which are painted guard ring electrodes, used to shim out higher-

order electric field components. The lower guard ring is split into halves to permit driving of the radial modes of the trapped ion. The trap has a minimum endcap-to-endcap spacing of 1.2 cm, and a minimum radius of 0.696 cm, giving an effective trap size $d = 0.549$ cm. The trap is inside a copper vacuum can, which cryoadsorbs to ultrahigh vacuum, but there is a line-of-sight path through a hole in the center of the upper endcap up the pumpout tube to a room-temperature gas-handling manifold. Ionizing electrons enter the trap from a field-emission point just below.

The ion's axial motion is detected via the image current induced in the upper endcap. The detection circuit includes a superconducting tank circuit ($Q = 25\,000$) and an rf SQUID.⁷ The real part of the detector's impedance damps the axial motion with a damping time $\tau_z = 6$ s. For a single ion pulsed to $\frac{1}{5}$ the trap size, the detector signal to noise ratio from 4 s of data is adequate to measure the axial frequency to 50 mHz and the phase to 15° .

The presence of even a single impurity ion has been observed to perturb the trap frequencies of the desired ion unacceptably. Ejecting impurity ions is a surprisingly difficult task. Our approach has been to heat the axial motion of impurity ions with band-limited white noise⁸ and then to lower ("dip") the voltage on the lower endcap, bringing the equilibrium position of the ion cloud very near the lower endcap. The more highly excited impurity ions are neutralized by striking the trap, leaving only the desired ion species in the trap. We use a similar dipping technique to thin the desired ions until only a single ion remains (Fig. 1).

The two radial ion modes do not couple to the detector and hence are undetected and undamped. In order both to cool these motions and to measure the all important cyclotron frequency, they must be coupled to the axial mode. We accomplish this with rf voltages applied across the halves of the lower guard ring at the sum or difference frequencies of the modes to be coupled.⁹⁻¹¹ To cool the magnetron motion we use the traditional sideband cooling scheme, a cw drive at $\nu_z + \nu_m$.¹⁰ But for cooling the cyclotron motion, and for precision mea-

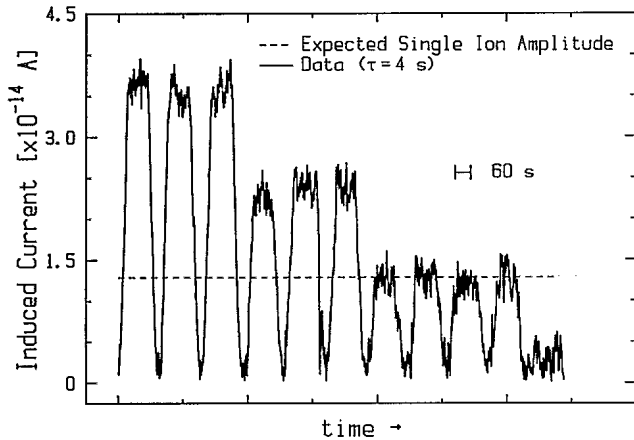


FIG. 1. Steps in the axial signals as one ion after another is expelled from the trap. The ions were driven to 20% of the trap size.

measurements of both the magnetron and cyclotron frequencies, we use a short pulse at the coupling frequency of two modes. A pulse with the appropriate amplitude-duration product (a “ π pulse”) will exchange the phase and action of one mode with those of the other.¹² To cool the cyclotron motion, we cool the axial motion resistively, and then use a π pulse to swap the cooled axial motion into the cyclotron mode. The caption of Fig. 2 describes how we use π pulses to measure the trap cyclotron and magnetron frequencies.

In order to measure the mass ratio of two ions, we alternate SICR measurements of the two ions under comparison—loading a CO^+ , measuring its frequencies, and then dumping it, and loading an N_2^+ ion, measuring its frequencies, and so on. Figure 3 shows the results of an evening of such measurements. Preparing a new ion for precision measurement, that is, loading a cloud of ions, ejecting the impurity ions, reducing the cloud to a single ion, and cooling the magnetron motion, requires at least 25 min. Any discontinuous field change, or even any dramatic change in the drift rate during this time will cause an error in the measured mass ratio.

Because our superconducting solenoid is only imperfectly self-shielding (85% efficient), changes in the ambient field are felt at the trap center. The data from run 3 were taken early in the morning, when the ambient magnetic noise was very low, and the scatter correspondingly small.

We observed frequency drifts over longer time scales that were evidently due to processes inside the apparatus. The drifts are affected by refilling the cryogenic fluids. We suspect they are caused at least in part by thermal expansion moving the trap center relative to the superconducting coils.

To extract a mass ratio from the data, we fit the magnetic field magnitude by a polynomial in time. The coefficients of that polynomial, and the CO^+/N_2^+ mass ratio, are the fit parameters. We fit the same data

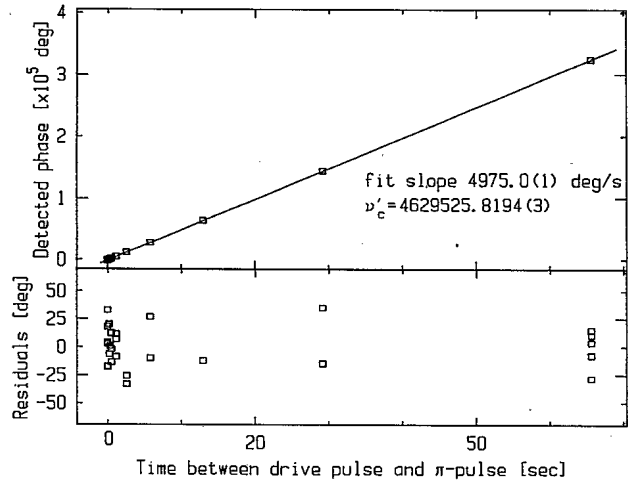


FIG. 2. For each plotted point, the following experiment is performed: The (initially cold) ion is pulsed into a cyclotron orbit of known initial phase, and then allowed to evolve “in the dark” for the indicated amount of time. Then a π pulse is applied, bringing the ion’s cyclotron action and phase into the axial mode. As the ion’s axial motion rings down, its phase is detected. The appropriate multiple of 360° is added, and a line is fitted to the points. The slope of the line is the offset from the frequency generator to the trap cyclotron frequency.

several times assuming, in turn, linear, quadratic, and cubic magnetic field temporal profiles. The data are seldom fitted any better by a cubic shape than by a quadratic shape, whereas the linear shape seems overly restrictive. In any event, the difference in the final mass-ratio results obtained from the different analyses is an informal measure of the price we pay for our ignorance of the temporal variation of the magnetic field. Combining the errors from the quadratic fits yields an overall error of

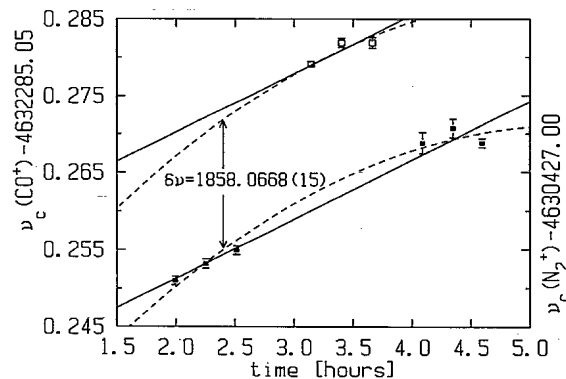


FIG. 3. The data from run 3 are shown. The solid squares are $\nu_c(\text{N}_2^+)$; the open squares are $\nu_c(\text{CO}^+)$. A total of three ions were loaded, in the order $\text{N}_2^+ - \text{CO}^+ - \text{N}_2^+$. The solid lines are a fit to the two frequencies assuming a field drift that is linear in time. The dotted-line fit assumes a quadratic field drift. The indicated value for $\nu_c(\text{CO}^+) - \nu_c(\text{N}_2^+)$ results from the latter assumption, and corresponds to $M(\text{CO}^+)/M(\text{N}_2^+) = 0.999\,598\,8876(3)$.

TABLE I. Determination of $M(\text{CO}^+)/M(\text{N}_2^+)$. The values listed in the table are the measured mass ratio $M(\text{CO}^+)/M(\text{N}_2^+) - 0.999\,598\,8800$, as fitted to the data from three different data runs, using three different polynomial forms for the time dependence of the magnetic field. The quoted error reflects the spread in the different fitting schemes, ± 0.2 ppb, and the typical "error" determined by assuming a given scheme, ± 0.3 ppb. Combined value: $0.999\,598\,8876(4)$.

Run	Fitting scheme		
	Linear	Quadratic	Cubic
1	84(9)	80(4)	74(6)
2	74(9)	75(8)	75(12)
3	72(3)	76(3)	77(3)
Average	73(3)	77(2)	76(3)

0.2 parts per 10^9 (ppb) (Table I). Our judgement is that 0.2 ppb is insufficiently conservative and our best estimate for $M(\text{CO}^+)/M(\text{N}_2^+)$ is $0.999\,598\,8876(4)$.

Although magnetic field uncertainties dominate our errors here, it is important to consider other sources of error which arise in this experiment. Many of these (e.g., effects which perturb the axial frequency) enter because the free-space cyclotron frequency $\omega_c = eB/mc$, which must be used to determine the mass ratio, is⁹

$$v_c^2 = v_c'^2 + v_z^2 + v_m^2, \quad (1)$$

where v_c' , v_z , and v_m are the measured trap frequencies. Equation (1) is exact even when the axis of the electrostatic field is not aligned with the magnetic field provided that the magnetic field is uniform and the electric field is a pure quadrupole. The hierarchy of frequencies, $v_c \gg v_z \gg v_m$, implies that for a desired final uncertainty ($\delta v_c/v_c$), we need to measure v_z to a much lower precision, and v_m to a still lower precision. In practice, we do not worry about any corrections to the magnetron frequency.

TABLE II. Error. The first column lists the major amplitude-dependent corrections to v_c' and v_z . The second column gives the effect of the corrections on v_c , to lowest order in the orbit radii. During the v_c' measurement, $a_c = 0.024(2)$ cm, $a_z = 0.005$ cm rms, and $a_m \lesssim 0.003$ cm. During the v_z measurement, $a_c \lesssim 0.002$ cm, $a_z = 0.120(7)$ cm, and $a_m \lesssim 0.003$ cm. The errors indicated are due to thermal motion or imperfect cooling. Because we measure a mass doublet, the value of the mean correction is not particularly important. Fluctuations (fourth column) put a limit on the accuracy attainable with a *single* pulse-and-phase measurement. The fifth column is an upper limit to the systematic dependence on ion species, for which we assume the driving and cooling pulses are constant to 1%. B_2 and C_4 , higher-order components of the magnetic and electric fields (Ref. 9), were compensated to $|C_4| \lesssim 5 \times 10^{-5}$ and $B_2 = 1.2(2) \times 10^{-6}$ cm⁻².

Correction (mode affected)	Form of $\Delta v_c/v_c$	Mean value of $\Delta v_c/v_c$	rms thermal error	Upper limit of systematic variation with ion species
Relativity (v_c')	$-\frac{1}{2}(\omega_c^2/c^2)a_c^2$	-2×10^{-10}	4×10^{-11}	5×10^{-12}
Electrostatic (v_c')	$\frac{3}{4}(C_4/d^2)(\omega_m/\omega_c)(-\frac{1}{2}a_c^2 + a_z^2 - a_m^2)$	2×10^{-11}	4×10^{-12}	5×10^{-13}
Electrostatic (v_z)	$\frac{3}{4}(C_4/d^2)(\omega_m/\omega_c)(-a_c^2 + \frac{1}{2}a_z^2 - a_m^2)$	5×10^{-10}	9×10^{-11}	1×10^{-11}
Magnetic (v_c')	$(B_2/2)(-a_c^2 + a_z^2 - a_m^2)$	-3.5×10^{-10}	6×10^{-11}	7×10^{-12}
Magnetic (v_z)	$(B_2/2)a_c^2$	3×10^{-12}	3×10^{-12}	1×10^{-13}

The finite sensitivity and nonzero temperature of our detector require the use of finite ion orbit radii a_c , a_z , and a_m . For finite radii, the measured frequencies are perturbed by the gradients in the magnetic field, the non-quadrupole components in the electric field, and special relativistic effects. The effects of these errors, which depend on various powers of the orbit radii, are summarized in Table II. The only systematic error which does not depend on the orbit radii is frequency pulling of ω_z due to coupling to the detector's tuned circuit, which causes a random error of less than 4×10^{-11} .

Clearly, the first obstacle to higher accuracy is temporal instability. While better engineering can stabilize the field somewhat^{13,14} a more elegant route to ultrahigh precision would be trapping one ion of each species to be compared and measuring them simultaneously. Preliminary theoretical and experimental work on the two-ion problem encourages our belief that ion-ion perturbations are controllable.¹⁵

We estimate that the troublesome field inhomogeneities B_2 and C_4 (which are higher-order spatial components of the magnetic and electric fields, defined in Ref. 9) can each be reduced by at least a factor of 10 by more careful shimming techniques, but relativistic mass shifts will limit accuracy to the 10^{-11} level unless there are improvements in cooling the cyclotron motion. Feedback cooling with a subthermal detector is a possibility. Also, under certain circumstances, one can win additional accuracy by deliberately distorting the magnetic field so as to cancel the relativistic correction to v_c' .

Mass comparisons at the 10^{-11} level and beyond will permit weighing molecular bonds and electronic binding energies. Measuring nuclei levels involved in γ -ray emission will give a value for the γ -ray energies in amu. This information, combined with a precise determination of γ -ray wavelength, would yield a new value for $N_A h$.¹⁶ $N_A h$, in turn, can be combined with a precise value for the electron mass, in amu, and with the Rydberg, to

determine an independent value for α^2 .

We would like to thank Deborah Kuchnir for technical assistance. This work was supported by the National Science Foundation (through Grant No. PHY86-05893 and a Graduate Fellowship to E.A.C.), and by the Joint Services Electronics Program Grant No. DAAL03-89-C-0001. G.P.L. thanks the donors of the Petroleum Research Fund. We are very grateful to R. Van Dyck for extensive helpful discussions.

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