Analysis and Elimination of Systematic Errors Originating from Coulomb Mutual Interaction and Image Charge in Fourier Transform Ion Cyclotron Resonance Precise Mass Difference Measurements

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The effect of mutual Coulomb-mediated interactions between ions of two different mass-to-charge ratios (but equal ion cyclotron orbital radii) on their Fourier transform ion cyclotron resonance (FT/ICR) mass spectral frequency difference is derived analytically and measured experimentally. For a cylindrical ion trap, ion packets are modeled theoretically as infinitely extended lines of charge, and contributions to cyclotron frequency difference due to direct Coulomb repulsion between the line charges as well as the forces arising from image charge induced on the trap electrodes by each line charge are calculated. A striking theoretical prediction is that the effect on ICR frequency difference of mutual Coulomb repulsion between ions in a mass doublet may be compensated by the image-charge effect. As a result, there is an optimal (calculable) ion cyclotron orbital radius at which the measured cyclotron orbital frequency difference between ions of two different mass-to-charge ratios is independent of mutual Coulomb-mediated interactions between the two components of the mass doublet! Moreover, if the two mass-doublet component ions are present in equal numbers, then the measured ion cyclotron orbital frequency difference is also independent of all Coulomb-mediated interactions between the two types of ions! Thus, the single largest systematic error in measurement of mass difference in a mass doublet by FT/ICR mass spectrometry may be virtually eliminated by appropriate control of ICR orbital radius and/or by performing measurements at various relative abundance ratios and extrapolating to equal relative abundance of the two mass-doublet components. We report experimental tests and verification of these predictions for two different mass doublets: $^3\text{He}^+ / ^3\text{H}^+$ (cylindrical trap at 4.7 Tesla) and $^{12}\text{C}^{12}\text{H}_2^+ / ^{14}\text{N}^+$ (cubic trap at 7.0 Tesla). From the latter measurement, we determine the mass of atomic nitrogen as $m(^{14}\text{N}) = 14.003\,074\,014(19)\text{ u}$. (*J Am Soc Mass Spectrom* 1993, 4, 855–868)

The potential of Fourier transform ion cyclotron resonance mass spectrometry (FT/ICR/MS) [1, 2] for precise mass measurement has long been recognized [3–5]. FT/ICR/MS may in fact offer the most precise method for measuring the mass difference between ions of two unlike mass-to-charge ratios (i.e., a mass “doublet”). The great advantages of FT/ICR are that ions of different mass may be trapped at the same spatial location, excited to the same cy-

clotron orbital radius, and detected simultaneously at extremely high-mass resolving power. Therefore, such effects as long-term drift of the magnetic field or variation of various experimental parameters with time and/or temperature, which restrict the precision of absolute frequency measurements, may be virtually eliminated in measurement of mass differences. Moreover, even moderate relative accuracy in a mass difference measurement may translate into extremely high accuracy for an absolute mass ratio determination. For example, our recent FT/ICR determination of the mass difference, $m(^1\text{H}_2\text{O}^+) - m(^2\text{HO}^+)$ [6], with relative imprecision of 8×10^{-6} (equivalent to 12 nu), corresponding to 6×10^{-10} imprecision for the mass ratio, $m(^1\text{H}_2\text{O}^+)/m(^2\text{HO}^+)$, compares favorably to the best

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prior published imprecision of 4×10^{-10} obtained for the mass ratio, $m(^{12}\text{C}^{16}\text{O}^+)/m(^{14}\text{N}_2^+)$, based on single-ion measurements with a compensated Penning trap [7].

Limits on mass accuracy in the FT/ICR measurement of the mass difference in a mass doublet arise principally from spatial and temporal inhomogeneity in the static magnetic field, nonquadrupolar electrostatic trapping potential, spatial inhomogeneity in the RF electric excitation field, Coulomb-mediated forces on the orbiting ion packet, and relativistic ion velocity [8-11]. Among these effects, the Coulomb-mediated forces arising from packets of ions of two different mass-to-charge ratios are the least characterized and understood. Systematic errors in precise mass measurement arising from direct ion-ion Coulomb repulsions and the Coulomb interaction between an orbiting ion packet and the image charge induced by that (or another) ion packet on the detection electrodes of the ion trap have been noted previously [8, 12], and were taken into account in prior FT/ICR/MS-based measurements of the $^3\text{H}^+/^3\text{He}^+$ mass difference [8, 13-15]. In this article, we consider the effects of Coulomb-mediated interactions on the mass difference determined from the ICR frequency difference between ions of two different mass-to-charge ratios.

In an early theoretical model for ion-ion Coulomb repulsion in ICR [16], an ion packet was modeled as a uniformly charged ellipsoid of revolution whose primary axis is coaxial with the magnetic field (and ion trap) symmetry axis (z-direction), leading to a quadrupolar electrostatic potential. Since a quadrupolar electrostatic potential leads to a particularly simple ion cyclotron frequency-to-mass relation [17], the ellipsoid model proved useful for moderately precise (~ 1 ppm) mass measurements over a wide mass range. However, the usual experimental situation during FT/ICR detection is that ions of interest are excited to approximately equal cyclotron orbital radii, and the remaining ions (which would otherwise reside on or near the z-axis) are ejected before detection. Therefore, more realistic recent descriptions consider orbiting ion packets modeled as points, disks, rings, or cylinders [18-20]. In a purely quadrupolar electrostatic trapping potential, mutual Coulomb repulsions between ions of the same mass-to-charge ratio do not shift the ion cyclotron orbital frequency [19, 21], but Coulomb repulsion between ions of unlike mass-to-charge ratios produces a net radially outward-directed force that opposes the Lorentz force from the applied magnetic field. As a result, the ion cyclotron frequency of ions of a given mass-to-charge ratio is shifted downward compared with the cyclotron frequency in the absence of Coulomb repulsions.

A second Coulomb-mediated effect is the shift in ion cyclotron orbital frequency arising from the attractive force between an ion and its image charge induced in the side (i.e., excitation and detection) electrodes of the ion trap (Figure 1). This force is also net radial

Figure 1. Schematic of the three Coulomb-mediated forces discussed in this article, for two ion packets of N_1 ions of mass-to-charge ratio m_1/q_1 , and N_2 ions of mass-to-charge ratio m_2/q_2 , orbiting about the symmetry axis of an applied magnetic field, B , at the same ion cyclotron radius, r . $F_{12}(r)$ is the direct Coulomb repulsion force on a given ion of type 1 from all ions of type 2. $F_{\text{ion 1-image 1}}$ (or $F_{\text{ion 1-image 2}}$) is the Coulomb force on an ion of type 1 from the image charge induced by all ions of type 1 (or type 2).

outward, and acts to lower the ion cyclotron orbital frequency (see Theory). The effect of image charge on ICR mass determination has previously been analyzed for an ion packet modeled as a point charge in a spherical capacitor [22], a line charge in an infinitely extended cylinder [23], and a point charge in a finite cylindrical or cubic trap [24].

We denote the three principal types of Coulomb-mediated interactions [8, 15] as "charge 1-charge 2" for direct ion-ion Coulomb repulsion, "charge 1-image 1" for the Coulomb attraction between ions of a given mass-to-charge ratio with the image charge induced by those same ions, and "charge 1-image 2" for the Coulomb attraction between ions of one mass-to-charge ratio with the image charge induced by ions of a different mass-to-charge ratio. The charge 1-charge 2 interaction does not depend on trap geometry, and prior treatments [19, 20] suffice for the present purpose. The charge 1-image 1 and charge 1-image 2 effects do depend on trap geometry, and we base (and justify) our analysis on ion packets modeled as line charges in an elongated cylinder [23] or in a cubic trap [24-27].

For the usual case that ions of two different mass-to-charge ratios have the same ion cyclotron orbital radius, we shall show that charge 1-image 2 interactions average to zero during a typical detection period. Next, although both direct ion-ion and ion-image charge interactions shift the ion cyclotron orbital frequency downward, we are able to show that both effects vanish for equal numbers of ions of two differ-

ent mass-to-charge ratios at the same cyclotron radius, because each ion cyclotron frequency is shifted (by charge 1-charge 2, and charge 1-image 1 or charge 2-image 2 interactions) by exactly the same amount. Finally, and less obviously, we show that the charge 1-charge 2 and charge 1-image 1 interactions produce opposite-sign shift (with opposite cyclotron radius dependence) in the ion cyclotron frequency difference between packets of ions of different mass-to-charge ratio but equal cyclotron radii. Thus, it is possible to choose an optimal cyclotron orbital radius at which the two effects cancel, even for unequal populations of the two types of ions! These predictions are tested experimentally on two mass doublets, $^3\text{He}^+ / ^3\text{H}^+$ (a close doublet, observed in a cylindrical trap at 4.7 Tesla) and $^{12}\text{C}^{12}\text{H}_2^+ / ^{14}\text{N}^+$ (a wide doublet, observed in a cubic trap at 7.0 Tesla). The latter measurement leads to a new and ultraprecise determination of the atomic mass of ^{14}N , with an accuracy comparable to the most accurate prior literature value.

Theory

Line Charge Model for Postexcitation Spatial Distribution of Ions

To choose an appropriate model for the ion charge distribution in the trap, we first need to have some idea of where the ions are located after dipolar radial (i.e., conventional) excitation [28]. We begin from an assumed axial (i.e., along the magnetic field z -direction) quadrupolar electrostatic trapping potential and a uniform electric excitation field perpendicular to the quadrupolar (z -) axis, both accurate to second-order in a Taylor expansion of the electric potential about the center of the trap. In this approximation, the electric excitation field does not create any work for ions moving in the z -direction. The equation of ion motion along the z -axis for an ICR ion trap of arbitrary geometry is defined by the trapping potential, V_T (eq 1) obtained by applying a potential, V_{tr} , to each of the two trapping electrodes.

$$V_T(r, z) = V_{tr} \left(\alpha_{tr} - \frac{\beta_{tr}}{\xi^2} (r^2 - 2z^2) \right) \quad (1)$$

in which ξ has dimensions of length and is a characteristic measurement of the size of the trap (e.g., for a cylindrical trap, ξ = trap radius), and the constants, α and β , are determined by the trap geometry [29-31]. For example, $\alpha_{tr}(\text{cubic}) = 0.33$ and $\beta_{tr}(\text{cubic}) = 1.39$; $\alpha_{tr}(\text{cylindrical}) = 0.28$ and $\beta_{tr}(\text{cylindrical}) = 0.45$ for a cylinder of unit aspect (length-to-diameter) ratio.

The energy of ion z -motion is conserved during dipolar radial (i.e., conventional) excitation. Because the electrostatic quadrupolar trapping potential flattens out along the z -direction as the ion cyclotron orbital radius, r , increases (see cross section through

Figure 2. Schematic cross-section through the $y = 0$ plane of a cylindrical ICR ion trap, cutting through the equipotential surfaces of the electrostatic trapping potential. Before cyclotron excitation (1), ions are bunched in a tight packet on the z -axis near the center of the trap. After cyclotron excitation (2), ions spread out until they reach the same value of the trapping potential. Thus, after cyclotron excitation, ions are well represented by a line-charge model (see text).

the $y = 0$ plane of the trap equipotential surfaces in Figure 2), a given ion's z -oscillation amplitude, z_0 , must therefore increase as r increases because the quadrupolar potential factor, $r^2 - 2z_0^2$, must remain constant:

$$\begin{aligned} z\text{-energy}(\text{total}) &= z\text{-energy}(\text{kinetic}) + z\text{-energy}(\text{potential}) \\ &= \text{constant} \\ &= E_z(\text{kinetic}) + E_z(\text{potential}) \\ &= qV_{tr} \left(\alpha_{tr} - \frac{\beta_{tr}}{\xi^2} (r^2 + 2z_0^2) \right) \end{aligned} \quad (2)$$

Stated another way, ions after excitation are able to roll "uphill" along the z -potential until they reach the same trapping potential as before excitation. Thus, as ions are excited radially to larger cyclotron orbits, they spread out along the z -direction, ultimately extending to the length of the trap along magnetic field direction when the postexcitation ion cyclotron radius reaches the radius of the trap.

More generally, it turns out that ion z -energy is conserved during radial excitation at the ion cyclotron frequency, even if the excitation electric field is spatially nonuniform. Dipolar radial ion cyclotron excitation increases the ion z -energy only when the excitation spectrum has a component at or near twice the trapping oscillation frequency [28, 31].

Next, we assume that the initial phases of ion z -oscillations are randomly distributed (as would be expected from electron ionization of a gaseous sample, or external ion injection of long duration compared with one trapping cycle). Thus, we may regard the distribution of ion charge along the z -axis as essen-

tially uniform before (and after) radial excitation. For example (see Figure 2), if the ions are evenly distributed within ~ 1 mm (in practice, probably somewhat wider [15]) along the z -axis of a 5.08 cm cubic trap before radial excitation, then they will be distributed within ~ 7 mm after excitation to a 1 cm cyclotron radius and within ~ 14 mm after excitation to a 2 cm cyclotron radius.

We also note that the initial ion spatial distribution is limited by the diameter (typically ~ 0.2 – 2 mm) of the ion-forming beam (e.g., electron ionization, photoionization) for ions formed inside the trap or by the ion beam diameter for externally injected ions. However, even if ions are initially distributed over a wide range of magnetron radii (i.e., a range of displacements from the z -axis), quadrupolar excitation may be employed to "axialize" the ions and squeeze them back into a narrow tube on the z -axis [32–35]. Ultimately, the ion radial distribution is limited by the thermal cyclotron radius (e.g., ~ 0.01 mm for C^+ ions at 7 Tesla).

Therefore, to a good approximation, we may model the postexcitation ion z -distribution as a line of charge uniformly distributed along the z -direction. Coulomb-mediated mutual interaction forces between ions may thus be taken to lie in a plane perpendicular to the trap z -axis, leading to great simplification in the theoretical analysis. Actually, the instantaneous interaction of an individual ion with the line of charge representing ions of a different mass-to-charge ratio depends on the instantaneous ion position because of the finite diameter of the line charge. The effect is to produce additional broadening (but not a frequency shift) of the ICR signal for the ions in question. We shall henceforth ignore this effect and treat only the interaction of a point charge with a line of charge.

Charge 1-Charge 2 Interactions

We begin by reviewing the direct Coulomb interaction between two parallel charged lines, representing a mass doublet of ions of two different mass-to-charge ratios, a problem previously treated by several authors [8, 19, 20] (see Figure 3). (Ions of a given mass-to-charge ratio do not shift each other's cyclotron frequency [21], unless the trapping potential is nonquadrupolar [19].) Chen and Comisarow [19] solved for the electric field (as a function of ion z -position) from a finite line of charge and then extrapolated to an infinitely extended line of charge. We begin from the electric field due to an infinitely extended line of charge,

$$E = \frac{\sigma}{2\pi\epsilon_0 d} \quad (3)$$

in which σ is the charge density (charge per unit length) along the line of charge, d is the perpendicular distance between the two lines of charge, and ϵ_0 is the permittivity of a vacuum. We may relate eq 3 to the

Figure 3. Relations between the ion-ion repulsion force, $F_{12}(r)$, or $F_{21}(r)$, and its radial component. The outwardly directed radial component effectively reduces the Lorentz force due to the applied magnetic field and shifts the ion cyclotron frequency downward. Note that $\cos \phi = \sin(\alpha/2)$, as derived in the text.

present problem by defining the charge density by dividing the actual total charge, $q_1 N_1$, by the actual length, l , of the line of charge in the trap,

$$\sigma = \frac{q_1 N_1}{l} \quad (4)$$

from which we obtain the electric field due to each line of charge,

$$E_1 = \frac{q_1 N_1}{2\pi\epsilon_0 dl} \quad (5a)$$

$$E_2 = \frac{q_2 N_2}{2\pi\epsilon_0 dl} \quad (5b)$$

in which q_1 and q_2 are the charges per ion, l is the length of the charged line, and N_1 and N_2 are the total numbers of ions constituting each charged line. The electrostatic force, F_{12} , acting on an individual ion in line 1 from all N_2 ions on the other line of charge is thus given by

$$F_{12} = \frac{q_1 q_2 N_2}{2\pi\epsilon_0 dl} \quad (6a)$$

and

$$F_{21} = \frac{q_1 q_2 N_1}{2\pi\epsilon_0 dl} \quad (6b)$$

It is the radial component of this force, $F_{12,\text{radial}}$ which affects the ion cyclotron frequency. From Figure 3,

$$F_{12}(r) = \frac{q_1 q_2 N_2}{2\pi\epsilon_0 dl} \cos \phi \quad (7a)$$

$$d = 2r \sin(\alpha/2) \quad (7b)$$

$$\alpha = 2\pi(\nu_{\text{eff},1} - \nu_{\text{eff},2})t \quad (7c)$$

in which $\nu_{\text{eff},1}$ and $\nu_{\text{eff},2}$ are “effective” ion cyclotron frequencies of the two mass-doublet components, r is the ion cyclotron orbital radius, and α is the cyclotron phase difference between the two orbiting line charges at time t , assuming that the lines were coincident at time zero. From the geometry of Figure 3, we see that $\cos \phi = \sin \frac{\alpha}{2}$, so that eqs 7a and b may be combined to yield

$$F_{12}(r) = \frac{q_1 q_2 N_2}{4\pi\epsilon_0 l r} \quad (8)$$

We therefore obtain the striking result that for the line-charge model, the radial component of the mutual Coulomb repulsion force between the ions (and thus the cyclotron orbital frequency shift—see below) is independent of the relative positions (i.e., cyclotron orbital phase difference between) of two line charges of the same cyclotron orbital radius!

Because the radial component of the Coulomb mutual repulsion force is exactly opposite in direction to the Lorentz force arising from motion of the ions in an applied magnetic field, it is convenient to represent the Coulomb mutual repulsion force as a small shift in the ion cyclotron frequency [19, 20]:

$$F_{12}(r) = m_1 r \omega_1 \delta\omega_1 = 2\pi q_1 B r \delta\nu_1 \quad (9)$$

in which B is the static magnetic field induction and $\delta\nu_1$ is the shift in ion cyclotron frequency of the first orbiting line of charge due to electrostatic interaction with the second orbiting line of charge. If ν_c and ν_m denote the unshifted cyclotron frequency ($qB/2\pi m$, in which m is ion mass) and the magnetron frequency [2, 36], then the “effective” ion cyclotron orbital frequency of the first type of ions is given by

$$\begin{aligned} \nu_{\text{eff},1} &= \nu_{c,1} - \nu_{m,1} - \delta\nu_1 \\ &= \nu_{c,1} - \nu_{m,1} - \frac{q_2 N_2}{8\pi^2 \epsilon_0 l B r^2} \\ &= \nu_{c,1} - \nu_{m,1} - \frac{2.3 \times 10^{-10} z_2 N_2}{l B r^2} \end{aligned} \quad (10)$$

in which z_2 is the number of elementary charges per ion of type 2. Note that eq 10 (like eq 8) is independent of the distance between the two line charges, unlike the more general case treated by Chen and Comisarow [19, 20] for a finite-extent line-charge model.

Finally, since the magnetron frequencies of two ions of approximately the same mass-to-charge ratio are virtually identical for ions of mass well below the “critical” mass [37], we may now write the error (systematic) in measurement of the difference in cyclotron frequency (from which the corresponding mass difference is obtained) between two components of a mass doublet,

$$\begin{aligned} \delta(\nu_{\text{eff},2} - \nu_{\text{eff},1}) &= (\nu_{\text{eff},2} - \nu_{\text{eff},1})_{\text{measured}} - (\nu_{c,2} - \nu_{c,1}) \\ &= \frac{(N_1 q_1 - N_2 q_2)}{8\pi^2 \epsilon_0 l B r^2} \\ &= \frac{2.3 \times 10^{-10} (N_1 z_1 - N_2 z_2)}{l B r^2} \end{aligned} \quad (11)$$

For example, for the $^3\text{He}^+ / ^3\text{H}^+$ mass doublet observed at $B = 4.7$ Tesla, $l \sim 1.0$ cm, and $r \approx 1$ cm (identical for both $^3\text{H}^+$ and $^3\text{He}^+$), the absolute systematic error is $\delta(\Delta\nu_{\text{eff}}) \approx 5 \times 10^{-5} (N_1 - N_2)$ Hz. Under these conditions, if $N_1 = 450$ and $N_2 = 550$ ions, the corresponding systematic error in measured mass difference is equivalent to ~ 0.5 eV difference in rest mass (mc^2) energy. At a cyclotron radius of 3 mm, the error is an order of magnitude larger. The most important and obvious feature of eq 11 is that the direct mutual Coulomb repulsion between two line charges does not affect the ICR-based mass difference measurement for a mass doublet, provided that an equal number of ions of each type is present.

Charge 1-Image 1 Interaction: Cylindrical Ion Trap

Nikolaev and Gorshkov [23] have previously analyzed the image charge induced in an infinitely extended conductive cylinder by a line of charge. For a line of charge of charge density (i.e., charge per unit length), σ_{ion} , and cyclotron orbital radius, r_{ion} , and its corresponding image charge of charge density, σ_{image} , and cyclotron orbital radius, r_{image} (see Figure 4, top),

$$r_{\text{ion}} r_{\text{image}} = r_{\text{trap}}^2 \quad (12a)$$

$$\sigma_{\text{ion}} = -\sigma_{\text{image}} \quad (12b)$$

in which r_{trap} is the radius of the cylindrical ion trap. From eq 12, the force (which is always radial in direction) acting on an ion of charge q , due to the image force from all N_1 ions, each of charge q , (see eq 6a) may be expressed as:

$$\begin{aligned} F_{\text{ion 1, image 1}} &= \frac{q_1^2 N_1}{2\pi\epsilon_0 l (r_{\text{image}} - r_{\text{ion}})} \\ &= \frac{q_1^2 N_1 r_{\text{ion}}}{2\pi\epsilon_0 l (r_{\text{trap}}^2 - r_{\text{ion}}^2)} \end{aligned} \quad (13)$$

Figure 4. Schematic of an ion packet and the force exerted by its corresponding image charge, relative to nearby cylindrical (top) or parallel-plate (bottom) electrodes.

resulting in a (downward) shift (see eq 9) in the ion cyclotron frequency to an effective frequency,

$$\begin{aligned} \nu_{\text{eff},1} &= \nu_{c,1} - \nu_{m,1} - \delta\nu_1 \\ &= \nu_{c,1} - \nu_{m,1} - \frac{q_1 N_1}{4\pi^2 \epsilon_0 l B (r_{\text{trap}}^2 - r_{\text{ion}}^2)} \end{aligned} \quad (14)$$

Finally, the contribution of the charge 1-image 1 interaction to the difference in observed effective cyclotron frequency for an infinitely extended cylindrical ion trap may now be expressed as

$$\delta(\nu_{\text{eff},2} - \nu_{\text{eff},1}) = \frac{(N_2 q_2 - N_1 q_1)}{4\pi^2 \epsilon_0 l B (r_{\text{trap}}^2 - r_{\text{ion}}^2)} \quad (15)$$

Charge 1-Image 1 Interaction: Parallel-Plate Detector

To obtain a rough estimate of the magnitude of the charge 1-image 1 interaction for a cubic trap, consider

the simplified model of an infinitely extended parallel-plate capacitor whose plates are perpendicular to the x -axis (Figure 4, bottom). The image charge parameters are then simply

$$\begin{aligned} r_{\text{image},1} &= a - 2x, & r_{\text{image},2} &= a + 2x, \\ \sigma_{\text{ion}} &= -\sigma_{\text{image},1} = -\sigma_{\text{image},2} \end{aligned} \quad (16)$$

in which $\sigma_{\text{image},1}$ and $\sigma_{\text{image},2}$ are the corresponding image charges, a is the distance between the plates, $r_{\text{image},1}$ and $r_{\text{image},2}$ are the distances from each line of charge to its corresponding image charge, and x is the instantaneous x -coordinate of the line of charge. For the geometry shown in Figure 4 (bottom), we may write for total radial force acting on an ion of charge q in one of the lines of charge

$$\begin{aligned} F_{\text{ion 1-image 1}}(\text{radial}) &= F_1(\text{radial}) - F_2(\text{radial}) \\ &= \frac{q_1^2 N_1}{2\pi \epsilon_0 l} \frac{4r \sin^2 \theta}{a^2 - 4r^2 \sin^2 \theta} \end{aligned} \quad (17)$$

in which r is the ion cyclotron radius and $\theta = 2\pi\nu_{\text{eff}}t$. For rapid circular ion motion, the time-averaged force

$$\begin{aligned} \langle F_{\text{ion 1-image 1}}(\text{radial}) \rangle &= \frac{1}{2\pi} \int_0^{2\pi} F_{\text{ion 1-image 1}}(r, \theta) d\theta \\ &= \frac{q_1^2 N_1}{2\pi \epsilon_0 l r} \left(\sqrt{\frac{a^2}{a^2 - 4r^2}} - 1 \right) \end{aligned} \quad (18)$$

leads to an effective ion cyclotron frequency

$$\begin{aligned} \nu_{\text{eff},1} &= \nu_{c,1} - \nu_{m,1} - \delta\nu_1 \\ &= \nu_{c,1} - \nu_{m,1} - \frac{q_1 N_1}{4\pi^2 \epsilon_0 l B} \frac{1}{r^2} \\ &\quad \times \left(\sqrt{\frac{a^2}{a^2 - 4r^2}} - 1 \right) \end{aligned} \quad (19)$$

Although the instantaneous force on the ions [20, 38] clearly varies with θ , the detection period is much longer than a period of the cyclotron motion. Thus, since the observed frequency shift represents a time integral of the instantaneous ion cyclotron phase, it is appropriate to integrate the observed force over θ to obtain eq 19. Finally, the contribution of the charge 1-image 1 interaction to the difference in observed effective cyclotron frequency for an infinitely extended parallel-plate capacitor approximation to a cubic ion trap may now be expressed as

$$\begin{aligned} \delta_S(\nu_{\text{eff},2} - \nu_{\text{eff},1}) &= \frac{(N_2 q_2 - N_1 q_1)}{4\pi^2 \epsilon_0 l B} \frac{1}{r^2} \left(\sqrt{\frac{a^2}{a^2 - 4r^2}} - 1 \right) \end{aligned} \quad (20)$$

For example, for the ${}^3\text{He}^+ / {}^3\text{H}^+$ mass doublet, under the conditions $l = 1$ cm, $B = 4.7$ Tesla, $r = 1$ cm, and $r_{\text{trap}} = 2$ cm (i.e., $a = 4$ cm), the ion cyclotron frequency shift (in Hertz) calculated from eq 20 is $\delta(\Delta\nu_{\text{eff}}) \approx 1.5 \times 10^{-5} (\Delta N)$. For example, if $N_2 - N_1 = 1000$ ions, then $\delta(\Delta\nu_{\text{eff}}) = 0.015$ Hz (corresponding to a mass difference error equivalent to ~ 2 eV in energy).

Charge 1-Image 2 Interactions: Cylindrical Ion Trap

We complete our analysis of Coulomb-induced shifts in ion cyclotron frequency by considering the interaction between ions of one mass-to-charge ratio with the image charge induced by ions of a second mass-to-charge ratio. We begin as before with an infinitely extended cylindrical ion trap. From the geometry shown in Figure 5 (top), the distance, h , between ions of type 1 and the image of ions of type 2 obeys the relation

$$h^2 = r_{\text{ion}}^2 + r_{\text{image 2}}^2 - 2r_{\text{image 2}}r_{\text{ion}} \cos \alpha \quad (21)$$

Figure 5. Schematic of two ion packets, and the force exerted by the image charge of one packet on an ion in the other packet, for cylindrical (top) and parallel-plate (bottom) electrodes.

in which α is the same as in eq 7. The radial component of the charge 1-image 2 interaction force then becomes

$$F_{\text{ion-image 2}}(\text{radial}, \alpha) = \frac{q_1 q_2 N_2}{2\pi\epsilon_0 l h} \cos \phi, \quad (22)$$

$$\cos \phi = \frac{r_{\text{image 2}}^2 - r_{\text{ion}}^2 - h^2}{2r_{\text{ion}} h}$$

From eqs 21 and 22 we obtain

$$F_{\text{ion-image 2}}(\text{radial}, \alpha) = \frac{q_1 q_2 N_2}{4\pi\epsilon_0 l r_{\text{ion}}} \frac{-2r_{\text{ion}}^2 + 2r_{\text{ion}} r_{\text{image 2}} \cos \alpha}{r_{\text{ion}}^2 + r_{\text{image 2}}^2 - 2r_{\text{ion}} r_{\text{image 2}} \cos \alpha} \quad (23)$$

Because the detection period is generally much longer than the cyclotron orbital period, we may average the force of eq 23 over all angles, $0 \leq \alpha \leq 2\pi$:

$$\langle F_{\text{ion-image 2}}(\text{radial}) \rangle = \frac{1}{2\pi} \int_0^{2\pi} F_{\text{ion-image 2}}(\text{radial}, \alpha) d\alpha = 0 \quad (24)$$

Thus, the interaction between ions of one mass-to-charge ratio and the image charge for ions of a second mass-to-charge ratio (but the same ion cyclotron orbital radius) does not result in a shift in ion cyclotron orbital frequency of either ion type (for the model of finite-length lines of charge in an infinitely extended cylindrical ion trap).

Charge 1-Image 2 Interactions: Parallel-Plate Detector

The result of eq 24 also holds true for a parallel-plate detector. Consider the charge 1-image 2 interaction for an infinitely extended parallel-plate capacitor (Figure 5, bottom) in a coordinate frame rotating at the ion cyclotron frequency, ω_2 , of the charged line type 2 ions. By symmetry, the initial phase of this rotation does not matter; we may therefore position the line of charge precisely midway between the two detection electrodes. For the geometry shown in Figure 5 (bottom), total radial component of the force acting on ions of type 1 from the image of the charged line of type 2 ions may be expressed as

$$F_{\text{ion 1-image 2}}(\text{radial}, \alpha) = \frac{q^2 N_2}{2\pi\epsilon_0 l} \left(\frac{(a-x)\sin \alpha + (r-y)\cos \alpha}{(a-x)^2 + (r-y)^2} - \frac{(a+x)\sin \alpha - (r-y)\cos \alpha}{(a+x)^2 + (r-y)^2} \right) \quad (25)$$

in which x and y are the instantaneous coordinates of the ion of type 1, a is the distance between electrodes, and r is the (common) cyclotron radius of both lines of charge. In cylindrical coordinates, $x = r \sin \alpha$ and $y = r \cos \alpha$, and the radial component of the force becomes

$$F_{\text{ion 1-image 2}}(\text{radial}, \alpha) = \frac{q^2 N_2}{2\pi\epsilon_0 l} \left(\frac{a \sin \alpha + r \cos \alpha - r}{(a - r \sin \alpha)^2 + (r - r \cos \alpha)^2} - \frac{a \sin \alpha - r \cos \alpha + r}{(a + r \sin \alpha)^2 + (r + r \cos \alpha)^2} \right) \quad (26)$$

As for the cylindrical trap, we may average over all α to obtain

$$\langle F_{\text{ion 1-image 2}}(\text{radial}) \rangle = \frac{1}{2\pi} \int_0^{2\pi} F_{\text{ion 1-image 2}}(\text{radial}) d\alpha = 0 \quad (27)$$

Thus, the interaction between ions of type 1 and the image charge from ions of type 2 does not lead to a systematic error in mass measurement, for ions of two mass-to-charge ratios orbiting at the same ion cyclotron radius, modeled as lines of charge between the plates of an infinitely extended parallel-plate capacitor.

Experimental

All $^{12}\text{C}^1\text{H}_2^+ / ^{14}\text{N}^+$ doublet experiments were carried out on a home-built FT/ICR mass spectrometer [39] consisting of a 7.0446 Tesla, 150 mm bore diameter superconducting solenoidal magnet (Oxford Instruments, Oxney Mead, England), a high-vacuum system with ten 300 L/s ion pumps and four titanium sublimation pumps (Perkin-Elmer TNB-X, Eden Prairie, MN), and an Extrel FTMS-2000 data station (Extrel FTMS/Millipore, Madison, WI) for control of the experimental event sequence as well as visualization, processing, and storage of mass spectral data.

The $^{12}\text{C}^1\text{H}_2^+$ and $^{14}\text{N}^+$ ion cyclotron resonances differ in frequency by 6932 Hz at 7.0446 Tesla. The following double-frequency excitation mode was used to excite both doublet components simultaneously [11]. The RF carrier frequency for ion cyclotron excitation was produced by a PTS-160 frequency synthesizer (100 kHz–160 MHz frequency range). In double-frequency excitation mode, the carrier signal at ν_{carrier} from the PTS 160 synthesizer was mixed with a 3466 Hz low-frequency signal produced by the Extrel FTMS-2000 data station synthesizer to produce a final excitation signal containing two frequency components $2 \times 3466 = 6932$ Hz apart. The excitation period was chosen to

be $\geq 500 \mu\text{s}$ to avoid overlap between these two components. The excitation signal after mixing was amplified and applied differentially to the excitation electrode plates of a 5.08 cm cubic ICR ion trap. The transient time-domain signal obtained by differential dipolar detection from a second pair of plates orthogonal to the first pair was amplified and mixed with a reference sinusoidal signal from another (PTS-40) RF frequency synthesizer. Ions were formed by electron impact ionization (40 eV electron beam for 100–300 ms at an emission current of $3.0 \mu\text{A}$ at 4×10^{-11} torr of a mixture of methane and molecular nitrogen). Ions were excited and detected by the use of a standard FT/ICR experimental event sequence: quench period of 10 ms, ion formation as described above, dipolar resonant axial ejection of unwanted ions ($^{12}\text{C}^+$, N_2^+), excitation (see above) of cyclotron motion of ions followed by a ~ 50 ms delay, and data acquisition (16 K time-domain data points, 2 kHz Nyquist bandwidth). The digitized time-domain unapodized data were then subjected to a fast Fourier transform and displayed in magnitude mode. The reference frequency was shifted by 300 Hz from the midpoint between the ICR frequencies for $^{12}\text{C}^1\text{H}_2^+$ and $^{14}\text{N}^+$ for convenience in display; the signal from $^{12}\text{C}^1\text{H}_2^+$ ions was detected by foldover [1, 40]. Figure 6 (top) shows a typical mass spectrum for this doublet, at a mass resolving power of 20,000,000 routinely used in these experiments. Peak heights were obtained by repeated zero-filling before FFT [41].

All experiments for the $^3\text{He}^+ / ^3\text{H}^+$ doublet were carried out on a CMS-47 (Spectrospin AG) FT/ICR mass spectrometer based on 4.686 Tesla, 150 mm bore diameter superconducting solenoidal magnet, a high-vacuum system with a 330 L/s turbomolecular pump (Balzers, Pfeiffer Turbo TPU 330, Zürich, Switzerland), and an Aspect-3000 data station for control of the experimental event sequence as well as visualization, processing, and storage of mass spectral data. Ions were formed by electron impact ionization (60 eV electron beam for 50–100 ms at an emission current of $\sim 1.0 \mu\text{A}$ at 5×10^{-9} torr of a mixture of helium-3 and molecular tritium). $^3\text{H}_2$ molecules were introduced into the vacuum system through a palladium inlet system cooled at liquid nitrogen temperature from a 1 Ci (12-year-old) sample.

At 4.7 Tesla, $^3\text{He}^+$ and $^3\text{H}^+$ ions have cyclotron frequencies of ~ 23.8 MHz, which exceeds the maximum frequency of the Spectrospin CMS-47 spectrometer. Excitation of cyclotron orbital motion was therefore produced by a home-built external high-frequency synthesizer. An RF carrier frequency signal at 20 MHz was mixed with a 3.8 MHz frequency signal produced by the Aspect-3000 data station synthesizer. After mixing, the final single-frequency excitation signal is centered midway between the helium-3 and tritium cyclotron frequencies. After mixing, the excitation signal was amplified and applied differentially to the excita-

Figure 6. Ultrahigh-resolution FT/ICR mass spectra of two mass doublets. Top: the widely spaced $^{12}\text{CH}_2^+ / ^{14}\text{N}^+$ doublet, detected at 7.0 Tesla in a 5.08 cm cubic ion trap. Bottom: the closely spaced $^3\text{He}^+ / ^3\text{H}^+$ doublet, detected at 4.7 Tesla in a 3.2 cm diameter, 5.0 cm long cylindrical ion trap. Because the heterodyne carrier frequency was placed between the $^{12}\text{CH}_2^+$ and $^{14}\text{N}^+$ cyclotron frequencies, the two peaks in the top spectrum are actually more widely separated than they appear in the figure.

tion electrodes of a cylindrical ICR ion trap (32 mm diameter, 50 mm long). The transient time-domain signal obtained by differential dipolar detection was amplified and mixed with a reference sinusoidal signal (20 MHz) from the same RF frequency synthesizer. Ions were excited and detected by the use of a standard FT/ICR experimental event sequence: quench period of 100 ms; ion formation as described above; axial ejection of unwanted ions by applying an RF voltage differentially between the trapping electrodes at the trapping frequencies of the unwanted ions, followed by a ~ 100 –500 ms delay; excitation of cyclotron motion of ions, followed by a ~ 20 –100 ms delay; and data acquisition (32 K time-domain data points, 1 kHz Nyquist bandwidth). The digitized time-domain data were then subjected to fast Fourier transformation and displayed in magnitude mode. Figure 6 (bottom) presents a typical mass spectrum for this doublet, at a mass resolving power of 10,000,000. Peak heights were obtained by interpolation with standard Bruker software.

Results and Discussion

From the theoretical expressions developed above for a Coulomb-mediated shift in ion cyclotron orbital frequency, we obtain two extremely useful predictions that should guide all future FT/ICR/MS-based measurements of mass difference between ions of unlike mass-to-charge ratios. We begin by combining the effects of both direct Coulomb repulsion and image-charge forces to obtain an expression for the overall shift in ion cyclotron orbital frequency difference between ions of two different mass-to-charge ratios:

$$\delta(\nu_{\text{eff},2} - \nu_{\text{eff},1})_{\text{cylindrical}} = \frac{(N_1 q_1 - N_2 q_2)}{4\pi^2 \epsilon_0 l B} \left(\frac{1}{2r_{\text{ion}}^2} - \frac{1}{r_{\text{trap}}^2 - r_{\text{ion}}^2} \right) \quad (28a)$$

for a cylindrical ICR trap and

$$\delta(\nu_{\text{eff},2} - \nu_{\text{eff},1})_{\text{parallel plates}} = \frac{(N_1 q_1 - N_2 q_2)}{4\pi^2 \epsilon_0 l B} \cdot \left(\frac{3}{2r_{\text{ion}}^2} - \frac{1}{r_{\text{ion}}^2} \sqrt{\frac{a^2}{a^2 - 4r_{\text{ion}}^2}} \right) \quad (28b)$$

for a cubic trap. Equation 28 is approximate and should in principle be modified for traps of finite aspect ratio [27, 31]; however, such effort is unwarranted because of the arguments advanced in the next two sections.

Coulomb-Mediated Frequency Shift Vanishes for Equal Abundances of Unlike Ions

It is obvious that there are two limits in which the Coulomb-mediated shift in ion cyclotron frequency (eq 28) vanishes, namely, when either the first or second bracketed term in either equation goes to zero. First, if $N_1 = N_2$ (i.e., equal numbers of ions of two unlike mass-to-charge ratios), then shifts induced by both ion-ion and ion-image charge vanish for either cylindrical or flat detection electrodes. Although it may not be easy experimentally to achieve the $N_1 = N_2$ condition in any one experiment, it is usually possible (e.g., by conducting electron ionization experiments at different partial pressures of the two components) to conduct a series of measurements at different relative abundances of the two types of ions and then extrapolate to the $N_1 = N_2$ limit (see below).

Optimal Ion Cyclotron Radius for Mass Difference Measurements: Theory

A second desirable situation is when the second bracketed expression in eq 28 vanishes. Note (see next paragraph) that the shift in ion cyclotron frequency difference is of opposite sign for the direct ion-ion repulsion than for the ion-image charge interaction.

Moreover, the ion-ion force decreases with increasing ion cyclotron radius, because the two ion packets (here modeled as lines of charge) are on the average farther apart at a larger cyclotron radius. However, the ion-image charge force increases with increasing ion cyclotron radius as the ion packet approaches the detection electrodes. Therefore, we obtain the very useful result that the overall Coulomb-mediated shift in ion cyclotron frequency vanishes at an intermediate "optimal" ion cyclotron orbital radius at which the ion-ion and ion-image charge forces exactly cancel! Setting the right-hand bracketed terms in eq 28 equal to zero quickly leads to

$$r \approx \frac{r_{\text{trap}}}{\sqrt{3}} \approx 0.6r_{\text{trap}} \quad (\text{cylindrical trap}) \quad (29a)$$

$$r = \frac{\sqrt{5}r_{\text{trap}}}{6} \approx 0.75\frac{a}{2} \quad (\text{cubic trap}) \quad (29b)$$

Figure 7 is an illustration of the effects described by eq 28. In the limit of a very small number of ions, Coulomb-mediated interactions produce negligible shift in ICR frequency, and the difference between cyclotron frequencies of two types of ions of different

mass-to-charge ratios is simply the difference in their "effective" cyclotron frequencies, that is, $\nu_2 - \nu_1 = \Delta\nu = \nu_{+,1} - \nu_{-,1}$, where $\nu_{+,1} = qB/2\pi m - \nu_m - \nu_{\text{relativistic}}$ = the ion cyclotron frequency, shifted by magnetron and relativistic terms. For unequal number ($N_1 > N_2$) of two such types of ions, $\nu_2 - \nu_1 < \Delta\nu$, because the dominant Coulomb-mediated frequency shift is from charge 1-charge 2 ion-ion repulsion, and the more abundant ions (N_1) shift the cyclotron frequency of the less abundant ions (N_2) more than vice versa. However, at a large cyclotron orbital radius approaching the diameter of the ion trap itself, the dominant Coulomb-mediated cyclotron frequency shift mechanism is charge 1-image 1 and charge 2-image 2 interactions, and $\nu_2 - \nu_1 > \Delta\nu$, because the more abundant ions (N_1) shift their own cyclotron frequency more than the less abundant ions (N_2) shift theirs. A little thought reveals that if $N_1 < N_2$, the same arguments apply, except that $<$ and $>$ are reversed in the above argument. Equation 29 represents the "optimal" ion cyclotron radius at which $\nu_2 - \nu_1 = \Delta\nu$, and the Coulomb-mediated frequency shift vanishes.

To demonstrate experimentally the effect of Coulomb-mediated (i.e., ion-ion and ion-image charge) interaction of ions of two different mass-to-charge ratios, we measured the ion cyclotron frequency difference as a function of the ratio between ion magnitude-mode peak heights, which are in turn approximately [42] proportional to the corresponding relative numbers of ions in the limit that the ICR response is linear [43, 44], and that the line shapes and widths of the two FT/ICR mass spectral peaks are the same. According to eq 28, the deviation of the difference in measured cyclotron frequencies of two unlike-mass ions from that observed in the absence of mutual Coulomb-mediated interactions between the two types of ions may be expressed as

$$\begin{aligned} \delta(\nu_{\text{eff},2} - \nu_{\text{eff},1}) &= (\nu_{\text{eff},2} - \nu_{\text{eff},1})_{\text{measured}} - (\nu_{c,2} - \nu_{c,1}) \\ &= f(r)N_2 \left(1 - \frac{N_1}{N_2}\right) \end{aligned} \quad (30)$$

in which $f(r)$ is an ion cyclotron radius-dependent function that depends on the ion trap configuration (see eq 28). A similar result follows from the ion packet model of Chen and Comisarow [19].

Establishment of Equal Cyclotron Orbital Radii for Ions of Two Different Mass-to-Charge Ratios

The present analysis requires that both types of ions have precisely the same cyclotron orbital radii. This condition was achieved experimentally by use of a short single-frequency excitation period (≤ 30 ms) for the closely spaced $^3\text{He}^+ / ^3\text{H}^+$ mass doublet [8, 14], so that ions of both masses were excited with the same RF voltage amplitude. For the more widely spaced $^{12}\text{C}^1\text{H}_2^+ / ^{14}\text{N}^+$ mass doublet, simultaneous excitation

Figure 7. Schematic of ion cyclotron frequencies, ν_1 and ν_2 , and ion cyclotron frequency difference, $\nu_2 - \nu_1$, for three different limiting situations relating to two ion packets of different mass-to-charge ratios but equal ion cyclotron orbital radius. As described in the text, ion-ion (middle plot) and ion-image charge (bottom plot) interactions have opposite effects on $|\nu_2 - \nu_1|$ relative to its unshifted value in the absence of Coulomb-mediated interactions (top plot).

at the two cyclotron frequencies was achieved by placing a carrier frequency exactly midway (to within a few megaHertz) between the two cyclotron frequencies, and modulating the frequency of the carrier to produce sideband excitation signals at each of the two ion cyclotron effective frequencies. (Relativistic shift during excitation [10] is negligible for this relatively high-mass doublet.) Because the number of trapped ions is expected to increase linearly with electron ionization period, the absence of any correlation (within the standard error of each measurement) between the measured difference in cyclotron frequencies and ionization period establishes that both components of the mass doublet have equal cyclotron orbital radii [14, 15] for both the $^3\text{He}^+ / ^3\text{H}^+$ (Figure 8, top) and $^{12}\text{C}^1\text{H}_2^+ / ^{14}\text{N}^+$ (Figure 8, bottom) mass doublets.

Experimental Cyclotron Frequency Difference as a Function of Ion Relative Abundance and Cyclotron Orbital Radius

Equation 30 predicts how cyclotron orbital frequency difference should vary with the relative abundance and cyclotron orbital radius of a population of trapped ions of two unlike mass-to-charge ratios. Figure 9 shows a typical dependence of the difference in experimentally measured cyclotron frequency between $^{12}\text{C}^1\text{H}_2^+$ and $^{14}\text{N}^+$ on the measured peak height ratio,

Figure 8. Ion cyclotron frequency difference for each of two mass doublets as a function of the duration of the period of electron ionization. Note the lack of dependence of cyclotron frequency difference on total number of trapped ions (see text).

$A(^{12}\text{C}^1\text{H}_2^+) / A(^{14}\text{N}^+)$. In these experiments, the ion relative abundances were varied by leaking in N_2 at a fixed rate, while varying the relative inlet leakage rate of CH_4 . Experiments of the type shown in Figure 9 were repeated at different cyclotron orbital radii, which were in turn calculated to third order in excitation potential [30]

$$\frac{r}{a} = 0.722 \frac{V_{(p-p)} t_{\text{excite}}}{2Ba^2} + 0.103 \left(\frac{V_{(p-p)} t_{\text{excite}}}{2Ba^2} \right)^3 \quad (31a)$$

for a cubic ion trap, in which a is the length of each side of the trap, $V_{(p-p)}$ and t_{excite} are the peak-to-peak RF amplitude and duration of the excitation electric potential, and

$$\frac{r}{d} = 0.883 \frac{V_{(p-p)} t_{\text{excite}}}{2Bd^2} - 0.023 \left(\frac{V_{(p-p)} t_{\text{excite}}}{2Bd^2} \right)^3 \quad (31b)$$

for a cylindrical trap of diameter d . As predicted by eq 30, the two straight lines in Figure 9 intersect at $N_1 = \text{N}_2$ (i.e., equal numbers of $^{12}\text{C}^1\text{H}_2^+$ and $^{14}\text{N}^+$ ions). Moreover, the ratio, 2.0, of the slopes of these two

Figure 9. Ion cyclotron frequency difference for the $^{12}\text{CH}_2^+ / ^{14}\text{N}^+$ mass doublet as a function of the ratio of the respective FT/ICR magnitude-mode mass spectral relative peak heights for experiments conducted at two different ion cyclotron orbital radii. Any Coulomb-mediated shift in the frequency difference is predicted to vanish when $A(^{12}\text{CH}_2^+) / A(^{14}\text{N}^+) = 1$, as evidenced by the intersection of the two best-fit straight lines at that peak height ratio (see text).

curves agrees with the value, $(2.2/1.5)^2 \approx 2.15$, predicted by eq 11. Figure 9 thus provides quantitative confirmation of the applicability of the line charge model for the cubic trap experiments reported here.

Optimal Ion Cyclotron Radius for Mass Difference Measurements: Experiment

Figure 10 shows the dependence of the slope of a plot of cyclotron frequency difference versus peak height ratio on ion cyclotron orbital radius, based on experimental data from $^3\text{He}^+ / ^3\text{H}^+$ in a cylindrical ion trap. As predicted by eq 28, there is an optimal intermediate cyclotron orbital radius at which ion-ion Coulombic repulsion between the two ion packets is exactly compensated by the ion-image charge attraction. At this radius, the measured cyclotron frequency difference (Figure 10) matches (to within the experimental standard deviation) that for the currently accepted mass difference between $^3\text{He}^+$ and $^3\text{H}^+$. The experimentally obtained optimal radius, $r_{\text{ion}} \approx 1$ cm (or $\sim 0.62 r_{\text{trap}}$), is in excellent agreement with that predicted analytically for a cylindrical trap ($r \approx 0.6 r_{\text{trap}}$) (eq 30a). For the cubic trap, the image-charge shift is predicted to appear only at $r_{\text{ion}} \geq 2.0$ cm, and we were unable to achieve sufficient S/N ratio at such a large ion cyclotron orbital radius ($r_{\text{ion}} \geq 2.0$ cm) due to z-ejection

of ions as well as the large relativistic shift and long excitation period used to detect this mass doublet.

Mass Measurement Accuracy: $^{12}\text{C}^1\text{H}_2^+ / ^{14}\text{N}^+$

A necessary condition for accurate mass measurements by FT/ICR/MS (or any other method) is that repeated measurements exhibit a Gaussian distribution, so that any remaining errors are random and may be reduced by statistical analysis of the repeated measurements. Figure 11 shows histograms describing the relative probability of a given ion cyclotron frequency difference between $^{12}\text{C}^1\text{H}_2^+$ and $^{14}\text{N}^+$, for experimental measurements in a 5.08-cm cubic ion trap at 7.0 Tesla. If Coulomb-mediated ion-ion and ion-image charge interactions are not taken into account (e.g., the relative abundances of the two ions may vary from one measurement to the next due to variation in relative leakage of the two gases through the sample inlets), then the histogram (Figure 11, top) is clearly non-Gaussian. However, if measurements are restricted to spectra for which the ratio of the abundances (as reflected by their relative magnitude-mode peak heights) is held constant at 1.00 ± 0.05 , then the histogram for

Figure 10. Plot of the slope of each of several graphs of the type shown in Figure 9, corresponding to each of several different ion cyclotron orbital radii. Note that the slope goes to zero (i.e., ion cyclotron frequency difference becomes independent of relative numbers of the two ionic components of a mass doublet) at the intermediate ion cyclotron radius calculated from eq 29 (see text).

Figure 11. Histograms of the relative probability of a given ion cyclotron frequency difference for the $^{12}\text{C}^1\text{H}_2^+ / ^{14}\text{N}^+$ mass doublet in a large number of repeated measurements. The upper plot represents experiments in which measurements were performed at various relative abundances of the two component ion types. The lower plot represents experiments in which the relative abundances of the two component ion types were kept equal for all measurements, as suggested by eq 30. Note the non-Gaussian distribution of the data in the upper plot, and the Gaussian distribution of the data in the lower plot (see text).

repeated measurements of the cyclotron frequency difference between $^{12}\text{C}^1\text{H}_2^+$ and $^{14}\text{N}^+$ (Figure 11, bottom) becomes Gaussian and statistical analysis of the data to recover an average frequency difference and standard deviation is possible. From such an analysis of the data in Figure 11b, we obtain the ion cyclotron frequency difference,

$$\nu_{\text{eff}}(^{14}\text{N}^+) - \nu_{\text{eff}}(^{12}\text{C}^1\text{H}_2^+) = 6932484.0(6.8) \text{ mHz} \quad (32)$$

corresponding to a mass ratio precision of 8.8×10^{-10} . The ion cyclotron orbital radius for these measurements was estimated as $2.1 \pm 0.1 \text{ cm}$, based on $V_{(p-p)} = 38 \text{ V}$, and $t_{\text{excite}} = 540 \mu\text{s}$. Uncertainty in cyclotron radius determination reflects the uncertainty between the radius determined by the use of the approximate eq 31 and the radius determined experimentally from the absolute relativistic shift [6, 10] in cyclotron frequency of $^{14}\text{N}^+$. The effective (measured) ion cyclotron frequency of $^{14}\text{N}^+$ ions was $7,725,724.05 \pm 0.01 \text{ Hz}$. In calculating the cyclotron frequency, we defined the magnetron shift as the slope in a plot of the measured cyclotron frequency of $^{14}\text{N}^+$ versus trapping potential: $25.2 \pm 0.3 \text{ Hz/V}$, or a magnetron shift, $\nu_m = 126.0 \pm 1.5 \text{ Hz}$, at the experimental electrostatic trapping potential of 5 V . The relativistic shift was $44.66 \pm 3.00 \text{ Hz}$ in absolute ion cyclotron orbital frequency and $120.3 \pm 8.1 \text{ mHz}$ in the difference in cyclotron frequency between $^{12}\text{C}^1\text{H}_2^+$ and $^{14}\text{N}^+$. From the above results, the $^{14}\text{N}^+$ cyclotron frequency as well as the difference in cyclotron frequencies between $^{12}\text{C}^1\text{H}_2^+$ and $^{14}\text{N}^+$ were corrected for magnetron and relativistic shifts to obtain

$$\nu_c(^{14}\text{N}^+) = 7,725,894.7 \pm 3.4 \text{ Hz} \quad (33a)$$

$$\nu_c(^{14}\text{N}^+) - \nu_c(^{12}\text{C}^1\text{H}_2^+) = 6,932,604.3 \pm 10.6 \text{ mHz} \quad (33b)$$

Other possible systematic errors connected with magnetic field drift ($\delta B/B \approx 8 \times 10^{-10} \text{ h}^{-1}$) and magnetic field inhomogeneity ($\delta B/B \approx 2 - 4 \times 10^{-7} \text{ cm}^{-1}$) were negligible [6]. Finally, the mass difference for the $^{12}\text{C}^1\text{H}_2^+ / ^{14}\text{N}^+$ ion doublet was calculated from the following expression

$$\begin{aligned} m(^{12}\text{C}^1\text{H}_2^+) - m(^{14}\text{N}^+) \\ = \frac{m(^{12}\text{C}^1\text{H}_2^+)}{\nu_c(^{14}\text{N}^+)} \{ \nu_c(^{14}\text{N}^+) - \nu_c(^{12}\text{C}^1\text{H}_2^+) \} \end{aligned} \quad (34)$$

in which the mass of $^{12}\text{C}^1\text{H}_2^+$ ion is already known to high accuracy [45] ($14.015101489(4) \text{ u}$), and we have used $548,580 \text{ nu}$ for the electron mass, 10.4 eV for ionization potential of CH_2 , 421.8 kJ/mol for the HC-H bond energy, 338.32 kJ/mol for the C-H bond energy, and a conversion factor of $0.01036 \text{ eV/(kJ/mol)}$

[46, 47]. For the mass difference in eq 36, we obtain

$$m(^{12}\text{C}^1\text{H}_2^+) - m(^{14}\text{N}^+) = 0.012576039(19) \text{ u} \quad (35)$$

and correspondingly for the mass of atomic nitrogen,

$$m(^{14}\text{N}) = 14.003074014(19) \text{ u} \quad (36)$$

in which we have taken 14.53 eV as the ionization potential of nitrogen [47]. The value in eq 36 is in good agreement with the previously accepted value, $m(^{14}\text{N}) = 14.003074002(26) \text{ u}$ [48], and with the value, $m(^{14}\text{N}) = 14.003074001(11) \text{ u}$, based on RF mass spectrometry [49].

Finally, based on the most recent and most accurate measurement of the mass ratio, $m(^{12}\text{C}^{16}\text{O}^+)/m(^{14}\text{N}_2^+) = 0.9995988876(4)$ [7], we can estimate the mass of atomic oxygen as,

$$m(^{16}\text{O}) = 15.994914638(27) \text{ u} \quad (37)$$

in excellent agreement with 1983 Atomic Mass Evaluation $15.994914630(50) \text{ u}$ [48]. In the present experiments, our use of a large-radius (5.04 cm cubic) trap required that measurements be conducted at a large ion cyclotron radius ($1.5\text{--}2 \text{ cm}$). As a result, the uncertainty in our final determination of the ^{14}N mass arises from uncertainty in ion cyclotron radius measurement (and corresponding uncertainty in ion velocity and relativistic shift in ion cyclotron frequency). (Measurement of ion cyclotron orbital radius from the ratio of third to first harmonic signal magnitude [23, 27, 50, 51] is difficult, because of the large difference in frequency between first and third harmonic.) Thus, the present mass accuracy could be improved by performing the experiments with a smaller-diameter trap.

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