*International Journal of Mass Spectrometry and Ion Processes*, 120 (1992) 71–83
Elsevier Science Publishers B.V., Amsterdam 

# Quadrupolar excitation and collisional cooling for axialization and high pressure trapping of ions in Fourier transform ion cyclotron resonance mass spectrometry

Lutz Schweikhard[1], Shenheng Guan and Alan G. Marshall[2]
*Department of Chemistry, 120 West 18th Avenue, The Ohio State University, Columbus OH 43210 (USA)*

(Received 30 January 1992)

ABSTRACT

A recently developed technique for axialization of ions in a Penning (i.e. hyperbolic) trap has been adapted for Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry in a dual cubic trap instrument. A resonant alternating electric azimuthal quadrupolar field at the combination frequency, $\omega_c = \omega_+ + \omega_-$, converts ion magnetron motion into collision-damped cyclotron motion. The usual collision-induced drift of ions from the center of the trap under the influence of the radially outward-directed electric force of the trapping field is thereby effectively inverted, so that ions with off-axis ICR orbit centers may be driven back to on-axis low radius ion cyclotron orbits. This effect is frequency-dependent and therefore mass-selective. The experiment requires only minor wiring modifications to an existing cubic, tetragonal, or cylindrical ICR ion trap. With this technique, we have been able to store benzene molecular ions for several seconds at high pressure ($>1 \times 10^{-5}$ mbar) in one half of a dual trap, as demonstrated by subsequent transfer of these ions to the other half of the dual trap for ICR excitation and detection. We also report simultaneous axialization and extended trapping of ions of different mass-to-charge ratios by use of multiple-frequency stored-waveform inverse Fourier transform excitation. Proposed applications include axialization and cooling for improved detection of product ions in MS–MS experiments, ion trapping at high pressure for extended periods for measurement of slow ion/molecule reaction rates, and increased sensitivity for detection of externally injected ions.

*Keywords*: ion trapping; collisional cooling; axialization.

## INTRODUCTION

Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry [1–10], also called FTMS, distinguishes itself from other mass analysis methods by its ultrahigh mass resolving power and high accuracy. These

*Correspondence to*: A.G. Marshall, Department of Chemistry, The Ohio State University, Columbus OH 43210-1173, USA.
[1] Ohio State University Postdoctoral Fellow; present address: Institute of Physics, University of Mainz, Standinger Weg 7, D-6500 Mainz, Germany.
[2] Also a member of the Department of Biochemistry.

0168-1176/92/$05.00 © 1992 Elsevier Science Publishers B.V. All rights reserved.

capabilities follow directly from the ability to trap ions for a long period [11]. Moreover, ion trapping also makes possible the determination of ion/molecule reaction pathways, kinetics, equilibria, and energetics, as well as multistage tandem mass spectrometry ($MS^n$) with a single-trap mass analyzer [12–14].

Another type of ion trap is the r.f. (or Paul) ion trap [15,16], in which an alternating quadrupolar electric field is used to spatially confine ion motion. Analytical r.f. ion traps are normally operated at millitorr helium pressure, at which ions undergo frequent collisions with neutrals and are thus prevented from leaking out of the trap owing to large-amplitude radial or axial oscillations. Because the ion motion is stable in all three spatial dimensions, ions are thereby trapped near the center of the trap and can be readily manipulated and removed for detection.

In an FT-ICR mass spectrometer, a strong magnetic field confines ion motion in a plane perpendicular to the magnetic field. Freedom of ion motion along the magnetic field is usually restricted by a static electric axial quadrupolar field. The combination of a uniform static magnetic field and a quadrupole electrostatic field leads to three separable types of ion motion: axial, cyclotron, and magnetron. In the presence of a high neutral gas pressure, the magnitudes of axial and cyclotron motions are both effectively reduced. However, a reduction in the energy of the magnetron motion is generally accompanied by an increase in magnetron radius, because magnetron potential energy decreases as magnetron radius increases, and ions are eventually lost radially. (In the presence of low-mass neutrals, high-mass ions excited to large coherent ion cyclotron orbital radii undergo ion/neutral collisions which slow but do not substantially change the direction of the heavy ions. Provided that their initial ion magnetron radii are negligibly small, such ions then spiral back to the center of the trap for re-excitation [17].)

In the fields of atomic, nuclear, and particle physics, cooling of charged particles in electromagnetic traps is vital to high precision measurements of the fundamental properties of the particles [18]. For an electron in a Penning trap (i.e. a hyperbolic ring electrode with two hyperbolic "end caps"), radiation by the electron can cool its cyclotron and axial motions efficiently. Resistive coupling of the induced current with an external circuit can be used to cool these motions for light ions as well. Unfortunately, these methods are not efficient for heavy ions, except when the number of trapped ions is very large [19]. The most effective method to cool heavy ions is by collisions with buffer gas [17,20], at the expense of some increase in magnetron radius with attendant radial loss of ions. However, the various ion motions can be coupled by excitation at various combination frequency modes. For example, Wineland and Dehmelt [21] first proposed the coupling of different modes of ion motion by means of sideband excitation.

The present work is based on a recently developed method for cooling of heavy ions [22–26] at the on-line Penning mass spectrometer [27–29] at ISOLDE/CERN [30]. The central idea of this method is that when ions are excited by an azimuthal quadrupolar field at the combination frequency, $\omega_c$

$$\omega_c = \omega_+ + \omega_- \tag{1}$$

i.e. the sum of the reduced cyclotron frequency, $\omega_+$, and the magnetron frequency, $\omega_-$, the magnetron motion can be converted completely into cyclotron motion [31]. $\omega_c$ is the unperturbed ion cyclotron orbital frequency in the absence of any electrostatic field:

$$\omega_c = \frac{qB}{m} \tag{2}$$

where $B$ is the applied state magnetic field induction, and $q/m$ is the ionic charge-to-mass ratio. $\omega_+ = \omega_c - \omega_-$ is the cyclotron orbital frequency which would be observed by conventional dipolar excitation and detection. For a comprehensive description of the ion motions and their corresponding frequencies see ref. 18. Since the cyclotron motion can be cooled very efficiently by the collision of ions with buffer gas molecules, one can achieve axialization (i.e. reduction of the magnetron radius) and cooling of the cyclotron motion (i.e. shrinkage of the ICR orbital radius) without attendant expansion of the magnetron orbit. The trapping motion is cooled as well.

In this work, we adapt and extend the above method in several ways. First, we employ broadband detection and Fourier transform data reduction, so as to be able to detect simultaneously ions of a wide range of mass-to-charge ratio, $m/q$. Second, in place of a single hyperbolic trap, we use a dual trap [32] with cubic geometry [33]. Finally, we use multiple-frequency excitation to axialize and cool ions of more than one $m/q$ ratio simultaneously. Specifically, ions are generated by electron impact ionization in the source trap and then axialized and cooled at high buffer gas pressure. The ions of interest are subjected to an azimuthal quadrupolar excitation field at their unperturbed ion cyclotron orbital frequency, $\omega_c$. The subscript "c" therefore holds a triple meaning: "cyclotron", "combination", and "cooling". Off-resonance ions will eventually be lost from the trap owing to the uncompensated collision-induced expansion of their magnetron orbits. After an extended irradiation period, the axialized cool ions are transferred to the analyzer trap where they can be detected at much lower pressure, thereby affording high mass resolution and all other advantages of FT-ICR MS [2]. If ions with different $m/q$ values are to be axialized and cooled, the quadrupolar excitation field must contain frequency components at $\omega_c$ for each $m/q$ value of interest. Extended trapping at high pressure of ions of one or more $m/q$ values is described below. We also report preliminary studies on the dependence of

trapping efficiency on quadrupolar excitation amplitude and frequency. In summary, by use of the dual-trap configuration, we are able to combine the advantages of quadrupolar excitation for ion axialization and cooling with all of the usual advantages of conventional FT-ICR dipolar excitation and detection.

## EXPERIMENTAL

All experiments were carried out on a standard Extrel FTMS-2000 spectrometer (Extrel FTMS, Madison, WI), equipped with Helix Technology CryoTorr-8 2000 $L\,s^{-1}$ cryopumps for both source and analyzer vacuum chambers, operated at a magnetic field of 3 T, and equipped with two 1.875 in cubic traps in a standard dual-trap configuration. Samples and collision buffer gases were admitted into the source side of the chamber through gold leaks in the batch inlet system of the instrument. Stored-waveform inverse Fourier transform (SWIFT) excitation waveforms were generated as described elsewhere [34].

Conventional azimuthal dipole excitation/dipole detection for the source trap was changed to azimuthal quadrupolar excitation geometry by connecting together the opposed conventional transmitting plates to provide one pair of transmit electrodes, and connecting together the opposed conventional receiving plates to form a second transmit electrode. The two pairs of opposed electrodes were then connected to the two differential (i.e. 180° phase difference) outputs of the standard excite amplifier (see Fig. 1 for wiring details). The cubic trap configuration provides a good approximation of the azimuthal quadrupolar excitation field near the center of the trap [35]. A trapping potential of $+5$ V or $+10$ V was used for all experiments.

The experimental event sequence is shown in Fig. 2. After ion generation by a low-energy ($\approx 15$ eV) electron beam, the ions of interest were subjected to a specified quadrupolar excitation time-domain waveform and held in the source trap by the combined effect of quadrupolar excitation and buffer gas cooling (see next section). Unwanted ions (i.e. those formed by the electron beam) were removed from the analyzer trap by a quench pulse to the analyzer trap plate (and/or by broadband radial ejection), and the cooled ions in the source trap were then transferred to the analyzer trap (by dropping the conductance limit potential to zero during the transfer period) for detection. Argon gas was used for ion cooling in the source trap. (Other gases have been tested for the Penning trap at ISOLDE/CERN and give similar results [36].) Sample pressure was $\approx 7 \times 10^{-8}$ mbar and the buffer gas pressure was kept at $\approx 2 \times 10^{-5}$ mbar (uncorrected readings from Bayard–Alpert gauges). The pressure at the analyzer trap was maintained at about $5 \times 10^{-8}$ mbar.

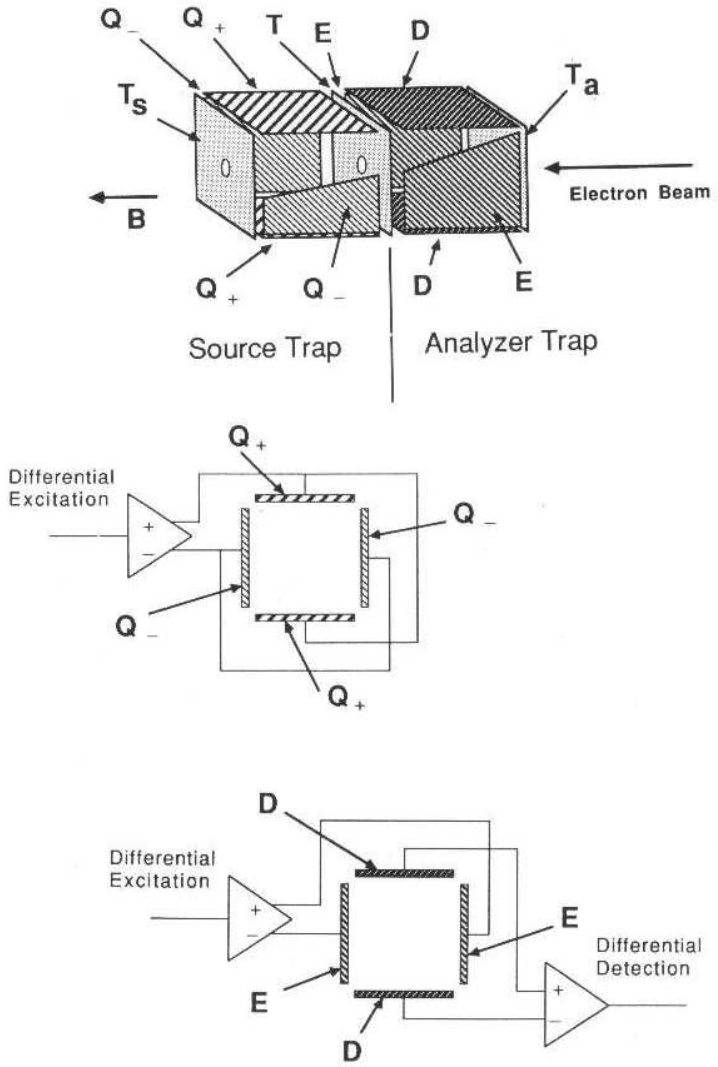


Fig. 1. FT-ICR MS dual cubic ion trap (top diagram), in which the source trap (whose midplane cross-section is shown in the middle diagram) is wired for azimuthal quadrupole excitation, and the analyzer trap (whose midplane cross-section is shown in the bottom diagram) is wired for conventional azimuthal dipole excitation on one pair of opposed plates and azimuthal dipole detection on the other pair of opposed plates. $T_s$: source-side trap plate; $T_a$: analyzer-side trap plate; T: conductance limit trap plate shared by source and analyzer; E: excitation plate; D: detection plate; $Q_+$, $Q_-$: plates used for azimuthal quadrupolar excitation.

## RESULTS AND DISCUSSION

### *Collision-induced ion radial loss*

Figure 3 (open circles) shows the relative magnitude-mode FT-ICR mass spectral peak height for benzene molecular ions ($m/q = 78$ u/$e$) as a function of trapping period in the source trap (i.e. delay period between ion formation and ion transfer to the analyzer trap). At a total pressure of $2 \times 10^{-5}$ mbar, ions undergo many collisions during the trapping period (several hundred collisions per second), leading to a rapid increase in ion magnetron radius. The rapid radial expansion of the ion cloud prevents subsequent transfer of

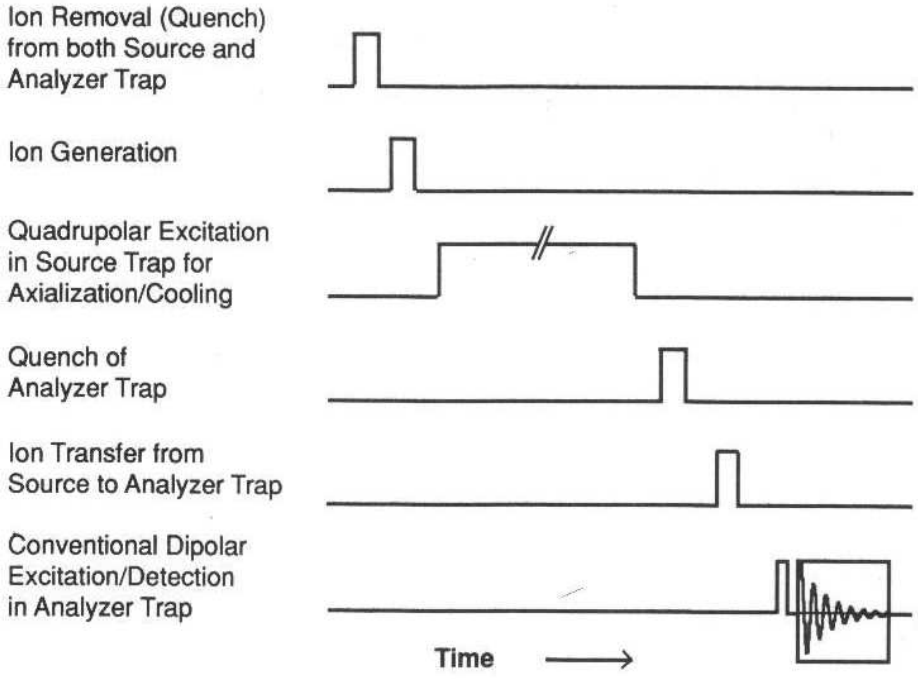


Fig. 2. Experimental event sequence for ion axialization/cooling experiments performed on the dual trap shown in Fig. 1. The removal of all positive ions from the analyzer trap before transfer of the ions of interest from the source trap may be achieved either by inversion of the voltage to the analyzer trap electrode, $T_a$, or by broadband radial ejection, or both in succession.

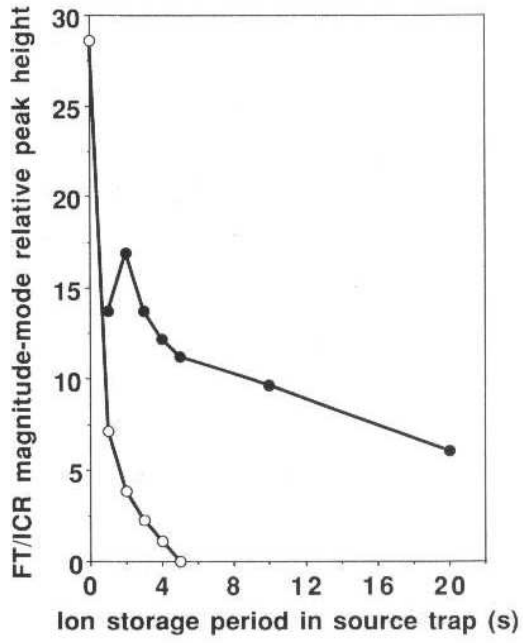


Fig. 3. Time evolution of analyzer trap FT-ICR magnitude-mode mass spectral peak height from benzene molecular ions, $C_6H_6^+$, without (open circles) and with (filled circles) prior azimuthal quadrupolar excitation in the source trap, as a function of storage period in the source trap. Each solid line simply connects the data points, and is included only to guide the eye.

these ions from the source trap (where they were created) to the analyzer trap, because the aperture between the two traps is smaller (2 mm diameter) than the average ICR magnetron radius. The ultimately detected ICR signal (in the analyzer trap) decreases approximately exponentially with increasing delay period between ion generation and ion transfer.

An understanding of the signal decay in this experimental set-up requires some knowledge of the ion distribution and its evolution in time. Ions generated by a thin electron beam of short duration are initially distributed homogeneously throughout a cylindrical volume along the applied magnetic field direction (i.e. the $z$ axis). However, ions formed near either trap plate have high potential energy, and speed up as they move "downhill" toward the center of the trap. Collisions quickly reduce the ion axial kinetic energy, so that ions relax (axially) to the center of the trap. The resulting increase in ion concentration and consequent increase in space charge repulsion then cause the ion cloud to expand radially. Since axial relaxation is much faster than radial expansion (i.e. increase in ion magnetron radius), the ion distribution immediately following axial relaxation can be represented as a two-dimensional disk in the trap midplane ($z = 0$). In the absence of a quadrupolar excitation field, the radius of the disk continues to increase beyond the radius of the conductance limit, and most of the ions will strike the conductance-limit plate of the trap during a subsequent attempt to transfer ions from the source to the analyzer side of the dual trap.

*Axialization produced by quadrupolar excitation and collisional cooling*

Detailed ion trajectory studies [25] show that the application of an azimuthal quadrupolar excitation field at the combination frequency, $\omega_c = \omega_+ + \omega_-$, can reduce the magnetron radius of a given ion, thereby effectively compressing the radius of the disk-shaped ion cloud. Most of the ions may then be transferred through the conductance limit, if the ion cloud is compressed to a radius smaller than that of the conductance limit. In the present experiments, we exploit the dual-trap configuration to monitor the evolution of the ion cloud and thereby evaluate the efficiency of ion axialization and cooling.

*Effect of quadrupolar excitation*

Figure 3 (closed circles) shows that application of an azimuthal quadrupolar excitation field at the combination frequency, $\omega_c = \omega_+ + \omega_-$, leads to successful trapping of benzene molecular ions for more than 20 s at a (high) pressure of $2 \times 10^{-5}$ mbar. The slow loss in signal with increasing ion storage period may be attributed at least in part to ion/molecule reactions. An ion

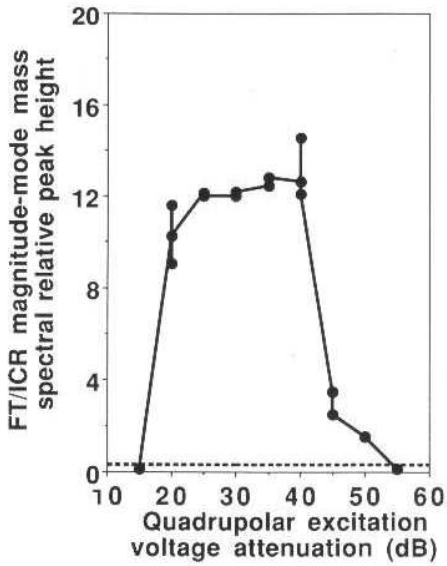


Fig. 4. Effect of azimuthal quadrupolar excitation amplitude on efficiency on ion axialization and cooling. The FT-ICR magnitude-mode mass spectral peak height measured for benzene molecular ions, $C_6H_6^+$, in the analyzer trap, is plotted as a function of relative quadrupolar excitation amplitude in 3 dB voltage increments (including some multiple measurements at the same attenuation) applied to the source trap. Thus, the actual quadrupolar r.f. excitation voltage varied from 0.2 V (55 dB attenuation) to 20 $V_{(p-p)}$ (15 dB attenuation). The solid line simply connects the data points, and is included only to guide the eye. The broken line denotes the r.m.s. magnitude-mode baseline noise level.

whose $m/q$ ratio changes by an ion/molecule reaction is lost from the trap because its $\omega_c$ value changes and the ion is thus no longer resonant with the quadrupolar excitation field. The same effect may be exploited with respect to mass selectivity (see below).

As noted above, the application of an azimuthal quadrupolar excitation field at frequency $\omega_c = \omega_+ + \omega_-$ involves both the cyclotron ($\omega_+$) and the magnetron ($\omega_-$) motions. Such excitation effectively converts magnetron motion into cyclotron motion and back again as discussed in detail in refs. 22–26 and 31: the higher the amplitude of the excitation field, the faster the interconversion. The trajectories of ions converge to the center of the trap in the presence of a buffer gas, provided that the quadrupolar excitation field is strong enough. Figure 4 shows a series of measurements where the attenuation of the quadrupolar excite signal has been varied. If the quadrupolar excitation field amplitude is too small (i.e. large attenuation), the conversion of magnetron and cyclotron motion is slow compared with collision-induced loss in magnetron energy (with corresponding increase in magnetron radius) and the ions are lost radially from the trap. Above a certain quadrupolar excitation amplitude threshold ($\approx 1\ V_{(p-p)}$), the conversion rate is fast enough to overcome the collision-induced loss in magnetron energy, and the ions can be kept in the center of the trap. Figure 4 shows that the relative number of

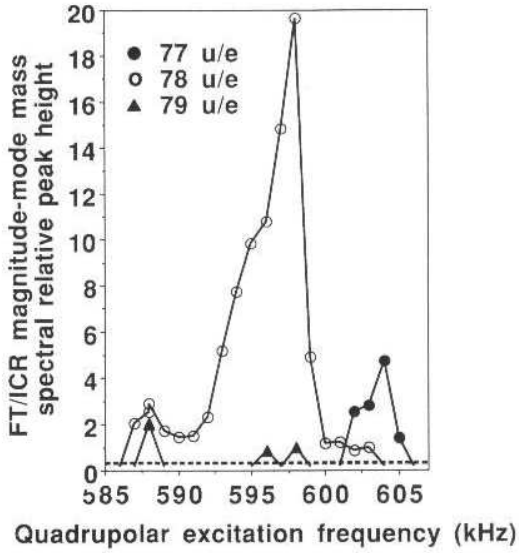


Fig. 5. Effect of azimuthal quadrupolar excitation frequency on the efficiency of axialization and cooling of ions derived from benzene. The FT-ICR magnitude-mode mass spectral peak height measured for benzene molecular ions, $C_6H_6^+$, in the analyzer trap, is plotted as a function of azimuthal quadrupolar excitation frequency, for $m/q = 77$ u/$e$ (●), 78 u/$e$ (○), and 79 u/$e$ (▲). See text for explanation of these results.

trapped ions is essentially independent of quadrupolar r.f. excitation voltage over an amplitude range of $\approx 25$ dB. Finally, at very high quadrupolar excitation amplitude ($\geqslant 12\,V_{(p-p)}$), ions are no longer effectively axialized, perhaps owing to instability of ion orbits under these conditions.

*Mass selectivity of the axialization process*

The axialization process is inherently mass-selective. For example, Fig. 5 shows how the axialization of ions of $m/q = 77$, 78, and 79 u/$e$ varies as the frequency of the azimuthal quadrupolar excitation field varies from 585 kHz to 607 kHz to span the cyclotron frequencies, $\omega_c$, of these ions. The low energy electron beam generates mainly $^{12}C_6H_6^+$ molecular ions (78 u/$e$), which are most effectively axialized at a quadrupolar excitation frequency corresponding to their ICR orbital frequency ($\approx 598$ kHz at 3.0 T). Similarly, $^{12}C_6H_5^+$ ions (77 u/$e$) are optimally axialized at a quadrupolar excitation frequency of $\approx 604$ kHz. Ions of $m/q = 79$ u/$e$ consist mainly of $^{12}C_6H_7^+$ formed by proton transfer, with a small proportion of $^{13}C^{12}C_5H_6^+$ molecular ions. At a quadrupolar excitation frequency of 588 kHz, both types of $m/q = 79$ u/$e$ ions are cooled and trapped. Interestingly, a small signal at $m/q = 79$ u/$e$ is observed on quadrupolar irradiation at the frequency ($\approx 597$ kHz) of the 78 u/$e$ molecular ion, $^{12}C_6H_6^+$; such a signal presumably arises from transfer of a proton from an axialized $^{12}C_6H_6^+$ ion to neutral $^{12}C_6H_6$.

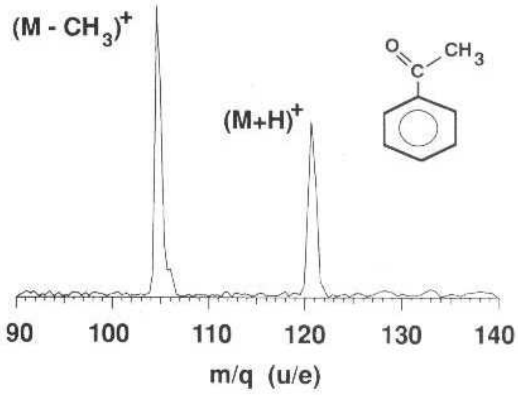


Fig. 6. FT-ICR magnitude-mode mass spectrum demonstrating the simultaneous axialization and cooling of ions of two different $m/q$ ratios. A SWIFT-generated azimuthal quadrupolar excitation voltage was applied continuously to the source trap during a storage period of 5 s at a buffer gas pressure of $\approx 2 \times 10^{-5}$ mbar before the protonated molecular ions ($m/q$ = 121 u/$e$) of acetophenone and its major fragment ($m/q$ = 105 u/$e$) were transferred to the analyzer side for conventional dipolar excitation and detection.

### *Axialization of ions of more than one* m/q *ratio*

Successful axialization clearly depends on resonant excitation at the combination frequency, $\omega_c = \omega_+ + \omega_-$. However, ions of different $m/q$ ratios may be axialized simultaneously, provided that the spectrum of the excitation field contains components at the $\omega_c$ values of the desired ions, as demonstrated experimentally in Fig. 6. Protonated molecular ions ($m/q$ = 121 u/$e$) of acetophenone and its major fragment ions ($m/q$ = 105 u/$e$) were simultaneously axialized and trapped by use of a SWIFT excitation signal containing components at the two combination frequencies corresponding to the two species.

### *Phase independence of axialization*

Several years ago, it was pointed out that the ion cyclotron radius of a spatially coherent ion packet may be reduced by driving the ions with a dipolar r.f. electric field that is 180° out of phase with the ICR orbital motion [37]. That effect was later used to develop two-dimensional FT-ICR MS [38–40], and also an "ion-lock" technique for near-instantaneous shrinkage of ICR orbital radius [41]. Moreover, in experiments superficially similar to those in this paper, ions with ICR orbital radii larger than the radius of the conductance limit of a dual trap were coherently (and mass-selectively) driven back to small ICR orbital radius for mass-selective transfer of ions from one side of a dual trap to the other [42,43]. However, all of the above experiments depend on initial cyclotron phase coherence of the ion packet. The present method holds no such limitation—axialization is independent of the initial magnetron or cyclotron phase of the ions.

*Projected applications*

It is important to note that the present method both axializes and cools ions. Initially cool (i.e. small ICR orbital radius) off-axis ions are brought on-axis with larger ICR orbital radii, and the ICR orbital radii then shrink as a result of collisions. Alternatively, hot (i.e. large ICR orbital radius) on-axis ions are cooled by collisions. In both cases, the quadrupolar field effectively holds ions on-axis as their cyclotron motion is converted to magnetron motion.

Ion axialization and cooling should prove especially valuable for increasing FT-ICR MS detection sensitivity of externally injected ions, which may have high axial velocity (compared with ions formed in the trap by electron ionization or chemical ionization) and/or off-axis initial position. The high axial velocity reduces ICR detection sensitivity [44] and degrades mass resolution [45]. With the new method, ion kinetic energy can be removed effectively without the usual radial ion loss owing to increase in magnetron radius. Trapping efficiency should thus be higher than for prior-gating trapping methods [46–49], because the present method not only reduces the axial velocity of the ions, but also reduces the radius of the ion cloud as well. The axialized cool ions may then be transferred with high efficiency from the source trap through a small conductance limit to the analyzer trap where they may be detected at much lower pressure (and thus higher sensitivity and mass resolving power). For example, matrix-assisted laser desorption is known to produce ions of approximately constant velocity, independent of mass [50], leading to severe reduction in detection sensitivity at high mass owing to high ion energy at high $m/q$ values [51]. The present method should be especially useful in facilitating FT-ICR trapping and detection of such species.

Applications of the present method to ion/molecule reaction chemistry include:

(i) Since ions can be cooled both internally and externally to the temperature of the neutrals, side reactions owing to high energy species can be eliminated.

(ii) The long trapping period at high pressure allows for many ion/neutral collisions and therefore makes possible the study of reactions with low ion/molecule reaction rate constants.

(iii) Monitoring of competing reactions can be "channeled" by trapping only the product ions of interest.

(iv) Product ions formed by off-axis collisions of cyclotron-excited parent ions with neutrals can be cooled and brought back on-axis for improved detection sensitivity and mass resolution. MS–MS performance for high mass ions (e.g. peptides) should be especially enhanced.

(v) Internally excited ions may be trapped long enough to undergo the very large number of collisions needed to thermalize their internal energy.

ACKNOWLEDGMENTS

This work was supported by N.S.F (CHE-9021058), N.I.H. (GM-31683), and The Ohio State University. L.S. thanks The Ohio State University and the Deutsche Forschungsgemeinschaft for post-doctoral fellowship awards.

REFERENCES

1 A.G. Marshall and P.B. Grosshans, Anal. Chem., 63 (1991) 215.
2 A.G. Marshall and L. Schweikhard, Int. J. Mass Spectrom. Ion Processes, 118/119 (1992) 37.
3 B. Asamoto and R.C. Dunbar, Analytical Applications of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, VCH, New York, 1991.
4 K.-P. Wanczek, Int. J. Mass Spectrom. Ion Processes, 95 (1989) 1.
5 C.L. Wilkins, A.K. Chowdhury, L.M. Nuwaysir and M.L. Coates, Mass Spectrom. Rev., 8 (1989) 67.
6 D.M. Lubman (Ed.), Lasers in Mass Spectrometry, Oxford University Press, New York, 1990.
7 M.V. Buchanan (Ed.), Fourier Transform Mass Spectrometry: Evolution, Innovation, and Applications, American Chemical Society, Washington, DC, 1987.
8 A.G. Marshall, Acc. Chem. Res., 18 (1985) 316.
9 S. Ghaderi, Ceram. Trans., 5 (1989) 73.
10 C.D. Hanson, E.L. Kerley and D.H. Russell, in J.D. Winefordner (Ed.), Treatise in Analytical Chemistry, Vol. 11, Wiley, New York, 1988, p. 117.
11 A.G. Marshall and F.R. Verdun, Fourier Transforms in NMR, Optical, and Mass Spectrometry: A User's Handbook, Elsevier, Amsterdam, 1990.
12 N.M.M. Nibbering, Acc. Chem. Res., 23 (1990) 279.
13 B.S. Freiser, in Bonding Energies in Organometallic Compounds, Vol. 428, American Chemical Society, Washington, DC, 1990, p. 55.
14 P. Sharpe and D.E. Richardson, Coord. Chem. Rev., 93 (1989) 59.
15 R.G. Cooks and R.E. Kaiser, Jr., Acc. Chem. Res., 23 (1990) 213.
16 J.F.J. Todd, Mass Spectrom. Rev., 10 (1991) 3.
17 E.R. Williams, K.D. Henry and F.W. McLafferty, J. Am. Chem. Soc., 112 (1990) 6157.
18 L.S. Brown and G. Gabrielse, Rev. Mod. Phys., 58 (1986) 233.
19 S.C. Beu, S.A. Hofstadler and D.A. Laude, Jr., Proc. 39th ASMS Conf. Mass Spectrometry and Allied Topics, Nashville, TN, 1991, p. 1534.
20 S. Maruyama, L.R. Anderson and R.E. Smalley, Rev. Sci. Instrum., 61 (1990) 3686.
21 D.J. Wineland and H.G. Dehmelt, Int. J. Mass Spectrom. Ion Phys., 16 (1974) 338.
22 G. Bollen, Ph.D. thesis, University of Mainz, 1989.
23 U. Wiess, Diploma thesis, University of Mainz, 1989.
24 L. Schweikhard, S. Becker, G. Bollen, H.-J. Kluge, G. Savard, H. Stolzenberg, U. Wiess and R.B. Moore, Proc. 38th ASMS Conf. Mass Spectrometry and Allied Topics, Tucson, AZ, 1990, p. 415.
25 M. König, Diploma Thesis, University of Mainz, 1991.
26 G. Savard, S. Becker, G. Bollen, H.-J. Kluge, R.B. Moore, L. Schweikhard, H. Stolzenberg and U. Wiess, Phys. Lett. A, 158 (1991) 247.

27 H.-J. Kluge, Phys. Scr., T22 (1988) 233.
28 S. Becker, G. Bollen, F. Kern, H.-J. Kluge, R.B. Moore, G. Savard, L. Schweikhard, H. Stolzenberg and ISOLDE Collaboration, Int. J. Mass Spectrom. Ion Processes, 99 (1990) 53.
29 H. Stolzenberg, St. Becker, G. Bollen, F. Kern, H.-J. Kluge, Th. Otto, G. Savard, L. Schweikhard, G. Audi and R.B. Moore, Phys. Rev. Lett., 65 (1990) 3104.
30 H.-J. Kluge, ISOLDE User's Guide, CERN Yellow Report 86-05, CERN, Geneva, 1986.
31 G. Bollen, R.B. Moore, G. Savard and H. Stolzenberg, Appl. Phys., 68 (1990) 4355.
32 D.P. Littlejohn and S. Ghaderi, US Patent 4,581,533, 1986.
33 M.B. Comisarow, Int. J. Mass Spectrom. Ion Phys., 37 (1981) 251.
34 A.G. Marshall, T.-C.L.Wang, L. Chen and T.L. Ricca, in M.V. Buchanan (Ed.), ACS Symp. Ser. 359, American Chemical Society, Washington, DC, 1987, p. 21.
35 P.B. Grosshans and A.G. Marshall, Int. J. Mass Spectrom. Ion Processes, 100 (1990) 347.
36 T. Otto, personal communication, 1991.
37 A.G. Marshall, T.-C.L. Wang and T.L. Ricca, Chem. Phys. Lett., 105 (1984) 233.
38 P. Pfändler, G. Bodenhausen, J. Rapin, R. Houriet and T. Gäumann, Chem. Phys. Lett., 138 (1987) 195.
39 P. Pfändler, G. Bodenhausen, J. Rapin, M.-E. Walser and T. Gäumann, J. Am. Chem. Soc., 110 (1988) 5625.
40 M. Bensimon, G. Zhao and T. Gäumann, Chem. Phys. Lett., 157 (1989) 97.
41 R. Chen, A.G. Marshall and M. Wang, Chem. Phys. Lett., 181 (1991) 168.
42 E.L. Kerley and D.H. Russell, Anal. Chem., 61 (1989) 53.
43 C.D. Hanson, E.L. Kerley and D.H. Russell, Anal. Chem., 61 (1989) 83.
44 R. Chen and P.B. Grosshans, unpublished results, 1992.
45 D.L. Rempel, R.P. Grese and M.L. Gross, Int. J. Mass Spectrom. Ion Processes, 100 (1990) 381.
46 J.M. Alford, P.E. Williams, D.J. Trevor and R.E. Smalley, Int. J. Mass Spectrom. Ion Processes, 72 (1986) 33.
47 D.A. Laude, Jr. and S.C. Beu, Anal. Chem., 61 (1989) 2422.
48 J.D. Hogan and D.A. Laude, Jr., Anal. Chem., 62 (1990) 530.
49 S.A. Hofstadler and D.A. Laude, Jr., Anal. Chem., 63 (1991) 2001.
50 R.C. Beavis and B.T. Chait, Chem. Phys. Lett., 181 (1991) 479.
51 T.D. Wood, L. Schweikhard and A.G. Marshall, Anal. Chem., 64 (1992) 1461.