Bloch equations applied to ion cyclotron resonance spectroscopy: Broadband interconversion between magnetron and cyclotron motion for ion axialization

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Conversion of magnetron motion to cyclotron motion combined with collisional cooling of the cyclotron motion provides an efficient way to reduce the kinetic energy of trapped heavy ions and to reduce their magnetron radii in an ion cyclotron resonance (ICR) ion trap. The coupling of magnetron and cyclotron motion can be realized by azimuthal quadrupolar excitation. Theoretical understanding of the coupling process has until now been based on resonant single-frequency quadrupolar excitation at the combination frequency $\omega_c = \omega_+ + \omega_-$, in which ω_c is the ion cyclotron orbital frequency in the absence of electrostatic field; and ω_+ and ω_- are the reduced cyclotron and magnetron frequencies in the presence of an electrostatic trapping potential. In this work, we prove that the magnetron/cyclotron coupling is closely related to a two energy level system whose behavior is described by the well-known Bloch equations. By means of a special transformation, the equations of motion for the coupling may be expressed in Bloch-type equations in spherical coordinates. We show that magnetron-to-cyclotron conversion by single-frequency quadrupolar excitation in ICR is analogous to a 180° pulse in nuclear magnetic resonance (NMR). We go on to show that simultaneous magnetron-to-cyclotron conversion of ions over a finite mass-to-charge ratio range may be produced by quadrupolar frequency-sweep excitation, by analogy to adiabatic rapid passage in magnetic resonance. Axialization by broadband magnetron-to-cyclotron conversion followed by cyclotron cooling is successfully demonstrated experimentally for a crude oil distillate sample.

INTRODUCTION

Fourier transform ion cyclotron resonance mass spectrometry (FT/ICR or FTMS) is a powerful analytical tool capable of ultrahigh mass resolving power, multistage MS/MS, high mass range, simultaneous detection of all ions, and long ion storage period, as described in recent reviews and ~250 references therein.[1,2] Trapping of ions in the presence of a strong magnetic field and a parallel approximately quadrupolar electrostatic field forms the foundation of all FT/ICR experiments. The magnetic field effectively confines ion motion in the plane perpendicular to the field. The freedom of ion motion along the magnetic field direction is restricted by an approximately quadrupolar electrostatic field. In the absence of excitation electric field, the ion trajectory can be analyzed into three independent cyclotron, magnetron, and axial motional components.

Ion-neutral collisions act to reduce the initial amplitudes of the cyclotron and axial motions, but increase the magnetron radius, because axial oscillation and cyclotron orbital kinetic energy each increase with increasing amplitudes of that motion, whereas the magnetron (mainly potential) energy decreases with increasing magnetron radius. Thus, ion-neutral collisions eventually lead to loss of ions from the trap when the sum of the cyclotron and magnetron radii exceeds the radius of the trap.

For ions of zero magnetron radius, collisions of heavy ions with light neutrals effectively damp the cyclotron orbit to near-zero, thereby "cooling" the ions and leaving them on or near the z axis (i.e., the magnetic field symmetry axis).[3] That process may be modeled as a frictional damping of ion cyclotron orbital velocity.[4–8] More generally, for ions with nonzero initial magnetron radius, the collision-induced increase in magnetron radius may be overcome by coupling the magnetron motion to either the cyclotron or axial motions.[9] For example, interconversion of magnetron and cyclotron motions may be achieved by use of azimuthal quadrupolar excitation at the unperturbed ion cyclotron orbital frequency $\omega_c = \omega_+ + \omega_-$, as demonstrated for ions of a single mass-to-charge ratio in a Penning trap[10,11] and more recently for ions of more than one mass-to-charge ratio in a dual cubic trap FT/ICR mass spectrometer.[12] Alternatively, we have also proposed a segmented cubic ICR trap configuration[13] to provide an excitation rf electric field of xz symmetry which couples magnetron motion to axial motion. Because the axial motion can be cooled efficiently by ion-neutral collisions, xz excitation in the presence of ion-neutral collisions provides yet another means for axial cooling and axialization of trapped heavy ions.

Although the above-cited methods for cooling and axializing trapped ions are attractive in principle, they employ temporally continuous time-domain excitation waveforms. However, the FT/ICR/MS experiment is inherently pulsed, consisting of a sequence of brief periods for ion formation and/or introduction into the trap, ion selection, ion-neutral reaction(s), excitation, detection, and ion removal. In this paper, we therefore introduce a pulsed-mode coupling of magnetron and cyclotron motion

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and examine the response of the coupling process to azimuthal quadrupolar excitation.

In a conventional FT/ICR excite/detect procedure, spatially coherent ion cyclotron orbital motion is excited by applying a differential excitation voltage between a pair of electrodes parallel to the magnetic field. Near the center of the trap, the excitation field can be approximated as a dipolar field and the equation of ion motion is linear. A linear response theory has recently been developed for dipolar excitation in the absence[14] and presence[15] of a static trapping potential.

In order to convert magnetron into cyclotron motion in a cubic ICR trap, the excitation electric field is generated by applying differential rf voltages differing in phase by 180° to two opposed orthogonal pairs of trap plates parallel to the magnetic field. Near the center of the trap, the excitation field can be approximated as an azimuthal quadrupolar field. The equations of ion motion are then no longer linear. The ion trajectory in response to single-frequency resonant excitation has been obtained previously.[10] However, it is necessary to extend the theoretical treatment to multiple-frequency excitation in order to achieve simultaneous cooling and axialization of ions whose mass-to-charge ratios span a wide range, as in typical analytical and chemical applications of FT/ICR/MS. Here we show that the equations of motion for the conversion process can be expressed as a special form of Bloch-type equations describing a system of two energy levels (i.e., analogous to a single spin 1/2 in magnetic resonance). It turns out that ICR magnetron and cyclotron motion can be described in quantum mechanical language.[9] In the absence of excitation and relaxation, they behave essentially like a harmonic oscillator. Both magnetron and cyclotron "oscillators" contain infinite numbers of energy levels. The azimuthal quadrupolar excitation acts as a combined raising and lowering operator to move one step up in a cyclotron (or magnetron) level, while simultaneously moving one step down in magnetron (or cyclotron) levels.

We begin by deriving the response to an azimuthal excitation potential in a cubic ICR ion trap. The equations of ion motion are conveniently expressed in terms of Brown and Gabrielse's "V vectors."[9] Introduction of a special transformation converts those equations to Bloch-type equations in spherical coordinates. Because the Bloch equations have been studied exhaustively in magnetic resonance spectroscopy,[16,17] we can adapt theoretical treatments for a two-level spin system to the coupling process between (e.g.) cyclotron and magnetron motions. For example, complete inversion of population in a range of resonance can be achieved by an adiabatic rapid passage (ARP) pulse.[18] Application of such a pulse allows a complete conversion from magnetron motion to cyclotron motion. In the presence of ion-neutral collisions (corresponding to spin relaxation in the magnetic resonance analogy), the cyclotron motion can be effectively damped and the reduction of the ion cloud radius simultaneously achieved. Experimental realization of pulsed-mode cooling and axialization is presented.

THEORY

Azimuthal quadrupolar potentials in a cubic ICR trap

In a cubic ICR trap configuration,[19] the static trapping potential Φ_{trap} can be expressed as

$$\Phi_{\text{trap}} = V_{\text{trap}}\left[\gamma - \frac{\alpha}{2a^2}(x^2+y^2-2z^2)\right], \tag{1}$$

in which V_{trap} is the trapping voltage applied to each trapping plate, a is the trap edge dimension, and γ and α are trap geometry factors; for a cubic trap, $\gamma=1/3$ and $\alpha=2.773\,73$, respectively.[20,21]

For azimuthal quadrupolar excitation, one needs to solve Laplace's equation subject to the following boundary conditions:

$$\Phi_{xy} = \begin{cases} V_{xy}(t), & x = \pm\frac{1}{2}a, \\ -V_{xy}(t), & y = \pm\frac{1}{2}a, \end{cases} \tag{2}$$

in which $V_{xy}(t)$ is the excitation voltage applied to the x electrodes and $-V_{xy}(t)$ is the excitation voltage applied to the y electrodes. It is convenient to analyze Φ_{xy} as the superposition of two potentials

$$\Phi_{xy}(x,y,z) = \Phi_1(x,y,z) + \Phi_2(x,y,z) \tag{3}$$

with boundary conditions

$$\Phi_1(x,y,z) = \begin{cases} 0, & y = \pm\frac{1}{2}a \text{ or } z = \pm\frac{1}{2}a, \\ V_{xy}(t), & x = \pm\frac{1}{2}a, \end{cases} \tag{4a}$$

and

$$\Phi_2(x,y,z) = \begin{cases} 0, & x = \pm\frac{1}{2}a \text{ or } z = \pm\frac{1}{2}a, \\ -V_{xy}(t), & y = \pm\frac{1}{2}a. \end{cases} \tag{4b}$$

Φ_1 and Φ_2 are thus antisymmetric with respect to the $x=y$ plane. Thus, to obtain the potential for the original geometry, we need only solve the Laplace equation for $\Phi_1(x,y,z)$ in the usual three-dimensional Cartesian coordinates

$$\nabla\Phi_1(x,y,z) = \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Phi_1(x,y,z) = 0. \tag{5}$$

Fortunately, the above boundary-value problem for an azimuthal (radial) quadrupolar potential is equivalent to that for the usual quadrupolar trapping potential in a cubic trap [Eq. (1)] with the substitution of the z axis by the x or y axis

$$\Phi_1(x,y,z) = V_{xy}(t)\left[\gamma - \frac{\alpha}{2a^2}(z^2+y^2-2x^2)\right] \tag{6a}$$

and

$$\Phi_2(x,y,z) = -V_{xy}(t)\left[\gamma - \frac{\alpha}{2a^2}(x^2+z^2-2y^2)\right]. \tag{6b}$$

Addition of Eqs. 6(a) and 6(b) gives

$$\Phi_{xy}(x,y,z)=\Phi_1(x,y,z)+\Phi_2(x,y,z)=\frac{3\alpha V_{xy}(t)}{2a^2}(x^2-y^2). \tag{7}$$

Ion motion subject to azimuthal quadrupolar excitation

The classical motion of the ion in a magnetic field **B** and electric field **E** subject to collisional damping force proportional to (and opposed in direction to) the ion velocity can be described by the modified Lorentz equation

$$m\dot{\mathbf{v}}=q(\mathbf{E}+\mathbf{v}\times\mathbf{B})-m\xi\mathbf{v}, \tag{8}$$

in which m and q are the mass and charge of the ion, and $\mathbf{v}$ $(=\dot{x}\mathbf{i}+\dot{y}\mathbf{j}+\dot{z}\mathbf{k})$ is its velocity. In FT/ICR experiments, **B** is constant and its direction can be used to define the z axis $\mathbf{B}=-B\mathbf{k}$. (**B** is taken to point in the negative z direction, so that the cyclotron orbital angular velocity of a positive ion is positive valued.) ξ is the collision damping frequency. The frictional damping ("relaxation") term $m\xi\mathbf{v}$ in Eq. (8) may be neglected during events short compared to $1/\xi$.

The electrical field is the superposition of the trapping and the azimuthal quadrupolar excitation fields; combining Eqs. (1) and (7) thus gives

$$\begin{aligned}\mathbf{E}&=-\nabla(\Phi_{\text{trap}}+\Phi_{xz})\\&=-\nabla\left\{V_{\text{trap}}\left[\gamma-\frac{\alpha}{2a^2}(x^2+y^2-2z^2)\right]+\frac{3\alpha V_{xy}(t)}{2a^2}(x^2-y^2)\right\}\\&=\frac{m}{2q}\omega_z^2(x\mathbf{i}+y\mathbf{j})-\frac{m}{q}\omega_z^2z\mathbf{k}-\frac{3\alpha V_{xy}(t)}{a^2}(x\mathbf{i}-y\mathbf{j}),\end{aligned} \tag{9a}$$

in which

$$\omega_z=\sqrt{\frac{2\alpha qV_{\text{trap}}}{ma^2}} \tag{9b}$$

is the axial or z-oscillation frequency. In the absence of collisional damping, substitution of Eq. (9) into Eq. (8) leads to independent equations for axial and azimuthal motion

$$\ddot{z}+\omega_z^2z=0, \tag{10a}$$

$$\ddot{\rho}-\omega_c\mathbf{k}\times\dot{\rho}-\tfrac{1}{2}\omega_z^2\rho+\phi_{xy}(t)(x\mathbf{i}-y\mathbf{j})=0, \tag{10b}$$

in which

$$\phi_{xy}(t)=\frac{3q\alpha V_{xy}(t)}{ma^2}, \tag{10c}$$

$$\rho=x\mathbf{i}+y\mathbf{j} \tag{10d}$$

is the azimuthal (radial) position vector, and

$$\omega_c=\frac{qB}{m} \tag{10e}$$

is the unperturbed cyclotron frequency in the absence of any electric field.

V-vector representation of equations of motion for magnetron/cyclotron conversion

As suggested by Brown and Gabrielse,[9] the azimuthal equation of motion (10b) can be further simplified by introduction of two vectors $\mathbf{V}^+$ and $\mathbf{V}^-$,

$$\mathbf{V}^+\equiv\dot{\rho}-\omega_-\mathbf{k}\times\rho, \tag{11a}$$

$$\mathbf{V}^-\equiv\dot{\rho}-\omega_+\mathbf{k}\times\rho, \tag{11b}$$

in which

$$\omega_\pm\equiv\frac{\omega_c}{2}\pm\sqrt{\frac{\omega_c^2}{4}-\frac{\omega_z^2}{2}}, \tag{11c}$$

ω_c is the unperturbed cyclotron frequency, ω_+ is the reduced cyclotron frequency, and ω_- is the magnetron frequency, $\mathbf{V}^+$ and $\mathbf{V}^-$ are seen to represent the cyclotron and magnetron velocities, including both the orbital motion in the absence of power absorption and the time rate of change of cyclotron and magnetron radii due to power absorption. $\mathbf{V}^+$ and $\mathbf{V}^-$ may be thought of as coordinates for cyclotron and magnetron motions treated as independent "normal modes." The position vector ρ and its derivative $\dot{\rho}$ may now be expressed as functions of $\mathbf{V}^+$ and $\mathbf{V}^-$,

$$\rho=-\frac{\mathbf{k}\times(\mathbf{V}^+-\mathbf{V}^-)}{\omega_+-\omega_-} \tag{12a}$$

and

$$\dot{\rho}=\frac{\omega_+\mathbf{V}^+-\omega_-\mathbf{V}^-}{\omega_+-\omega_-}. \tag{12b}$$

The azimuthal equations of motion then become

$$\frac{dV_x^\pm}{dt}+\omega_\pm V_y^\pm+\frac{\phi_{xy}(t)}{\omega_+-\omega_-}(V_y^+-V_y^-)=0, \tag{13a}$$

$$\frac{dV_y^\pm}{dt}-\omega_\pm V_x^\pm+\frac{\phi_{xy}(t)}{\omega_+-\omega_-}(V_x^+-V_x^-)=0. \tag{13b}$$

Finally, by representing the x and y components of the cyclotron and magnetron velocities as real and imaginary parts of mathematically complex velocities V^+ and V^-,

$$V^+=V_x^++iV_y^+, \tag{14a}$$

$$V^-=V_x^-+iV_y^-, \tag{14b}$$

we may combine Eqs. (13) and (14) to obtain

$$\frac{dV^+}{dt}-i\omega_+V^++i\frac{\Omega(t)}{2}(V^{+*}-V^{-*})=0, \tag{15a}$$

$$\frac{dV^-}{dt}-i\omega_-V^-+i\frac{\Omega(t)}{2}(V^{+*}-V^{-*})=0, \tag{15b}$$

in which

$$\Omega(t)=\frac{2\phi_{xy}(t)}{\omega_+-\omega_-}=\frac{6q\alpha V_{xy}(t)}{ma^2(\omega_+-\omega_-)} \tag{15c}$$

and

$$V^{+*}=V_x^+-iV_y^+, \quad V^{-*}=V_x^--iV_y^-. \tag{15d}$$

If only the conversion between magnetron and cyclotron motion is considered, V^{+*} may be neglected in Eq. (15a) and V^{-*} may be neglected in Eq. (15b), since V^{+*} (or V^{-*}) rotates in the opposite sense as V^+ (or V^-) [i.e., is "off resonance" by $2\omega_+$ (or $2\omega_-$)]

$$\frac{dV^+}{dt}-i\omega_+V^+-i\frac{\Omega(t)}{2}V^{-*}=0, \tag{16a}$$

$$\frac{dV^-}{dt}-i\omega_-V^-+i\frac{\Omega(t)}{2}V^{+*}=0. \tag{16b}$$

Relation of magnetron/cyclotron conversion with a two-level system

Integration of Eqs. (16) reveals that

$$|V^+|^2+|V^-|^2=C, \tag{17}$$

in which C is a constant determined by the initial conditions. The conservation of $|V^+|^2+|V^-|^2$ suggests that it is possible to introduce the following transformation for the normalized V vectors {i.e., divide V^+ and V^- by $\sqrt{C}$, and recall that $[\sin^2(\theta/2)+\cos^2(\theta/2)=1]$}

$$V^+=\sin(\theta/2)e^{i\psi_+}, \tag{18a}$$

$$V^-=\cos(\theta/2)e^{i\psi_-}, \tag{18b}$$

in which ψ_+ and ψ_- are the phases and $\sin(\theta/2)$ and $\cos(\theta/2)$ are the amplitudes of V^+ and V^-, respectively. If θ is confined to the range $0\leqslant\theta\leqslant\pi$, then the amplitudes are always positive valued. Equations (16) may now be combined to yield

$$\left[\frac{d\theta}{dt}\cos\theta+i\left(\frac{d\phi}{dt}-\omega\right)\sin\theta\right]e^{i\phi}=i\cos(\theta)\Omega(t) \tag{19a}$$

with

$$\phi=\psi_++\psi_-, \tag{19b}$$

$$\omega=\omega_++\omega_-=\omega_c. \tag{19c}$$

Equations (19) may now be recognized as a form of the Bloch equations expressed in spherical coordinates for a two-level system [see Guan's Eq. (13) (Ref. 22)]. The magnetic field is defined along the negative z axis, leading to counterclockwise rotation of ω_+ and ω_-.

EXPERIMENT

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 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. Argon gas was admitted into the source side of the chamber through a Varian leak valve installed on the batch inlet system, in order to provide for ion-neutral collisions to cool the cyclotron orbital motion (see Results and Discussion).

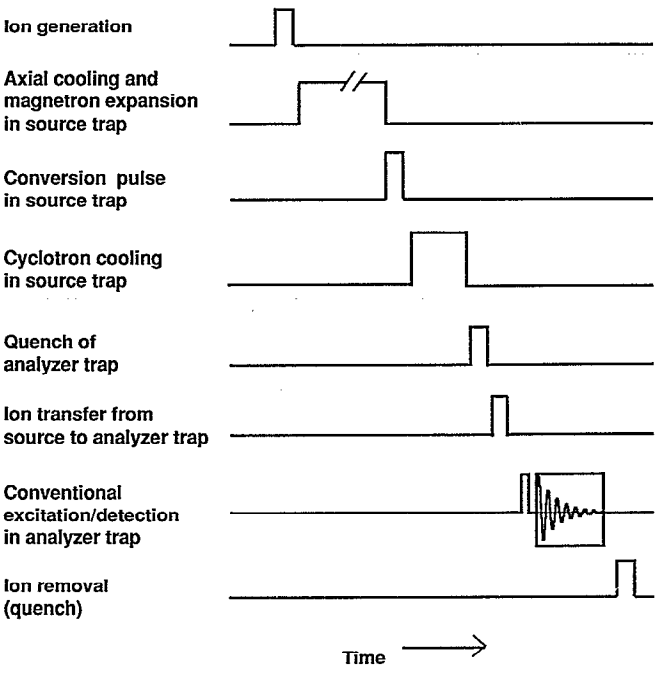

FIG. 1. Experimental event sequence for pulsed-mode magnetron/cyclotron conversion, ion cooling, and axialization experiments in an ICR dual ion trap. Following ion formation in the source trap, a period of a few seconds allows for the relaxation of axial motion and expansion of magnetron motion. After subsequent conversion of magnetron to cyclotron motion, a relaxation period of a few tens of milliseconds allows for collisional cooling of the cyclotron motion, so that ions are axialized before transfer to the analyzer trap. Ions are then excited and detected in the analyzer trap.

Crude oil fractions from Amoco were introduced into the FT/ICR spectrometer through a heated glass inlet system (Brunfeldt Co., Bartlesville, OK). Argon gas was used for ion cooling in the source trap. Generation of the azimuthal quadrupolar excitation in the source trap was as described by Schweikhard *et al.*[12] Trapping potential was +10 V for all experiments.

The experimental event sequence is shown in Fig. 1. Following ion generation by an electron beam, a time period was provided for relaxation of the initial axial and cyclotron motions. If the period is sufficiently long, the magnetron radius expansion could be observed. The ions of interest were then subjected to a quadrupolar excitation pulse synthesized for complete conversion of magnetron motion to cyclotron motion (see the Theory section). The cyclotron motion of the converted ions was cooled by ion-neutral collisions with the buffer gas, and the ion cyclotron orbital radii of ions of various m/q values were thereby reduced. 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 subsequent excitation and detection. Sample pressure was $\sim 5\times10^{-8}$ Torr and the buffer gas pressure was kept above 2×10^{-5} Torr (specified where appropriate). The pressure at the analyzer trap was maintained below 1×10^{-7} Torr.

RESULTS AND DISCUSSION

Conservation of ion cloud radius

An important consequence of Eq. (17) is that the radius of the ion cloud is not changed by a pulse which completely converts magnetron motion into cyclotron motion. Suppose that the ions begin with a finite magnetron radius and zero cyclotron orbital radius cyclotron $V^+(0)=0$; $V^-(0)=V^-_{\text{initial}}$ at time 0. Further suppose that a suitable pulsed excitation converts the magnetron motion completely into cyclotron motion after a time period T: $V^+(T)=V^+_{\text{final}}$; $V^-(T)=0$. According to Eq. (12a), the radius of the ion cloud is described before excitation by the magnetron radius and after excitation by the cyclotron orbital radius

$$r_{\text{initial}}=\frac{|V^-_{\text{initial}}|}{\omega_+-\omega_-} \tag{20a}$$

and

$$r_{\text{final}}=\frac{|V^+_{\text{final}}|}{\omega_+-\omega_-}. \tag{20b}$$

From Eq. (29), we have

$$|V^+_{\text{final}}|=|V^-_{\text{initial}}|. \tag{21}$$

Therefore, the postexcitation (cyclotron) radius of the ion cloud (r_{final}) is equal to its preexcitation (magnetron) radius

$$r_{\text{final}}=r_{\text{initial}}. \tag{22}$$

Pulsed single-frequency cooling and axialization

For single-frequency quadrupolar circularly polarized excitation, we may express $\Omega(t)$ in Eq. 15(c) as

$$\Omega(t)=\Omega_0 e^{i\omega t}, \tag{23a}$$

in which

$$\Omega_0=\frac{3q\alpha V_{xy}(0)}{ma^2(\omega_+-\omega_-)}. \tag{23b}$$

For resonant single–resonant quadrupolar excitation, $\omega=\omega_c$. By analogy to the two-level Bloch treatment of magnetic resonance for spin one-half particles, $\Omega_0=d\theta/dt$, the frequency of oscillation between pure magnetron and pure cyclotron motion, is analogous to the frequency of rotation of the magnetic moment about the effective field in the rotating frame. Thus, single-frequency resonant quadrupolar excitation applied for a period τ, such that $\Omega_0\tau=\pi$ radians, converts (e.g.) pure magnetron motion into pure cyclotron motion, and is analogous to a single-frequency resonant 180° pulse in nuclear magnetic resonance (NMR). We shall therefore henceforth denote such an excitation as a "π pulse."

Pulsed-mode cooling and axialization is illustrated in Fig. 2 for single-frequency quadrupolar excitations of ions of a single mass-to-charge ratio. Within a few tens of milliseconds after ion formation (say, by electron impact of a gaseous sample), the ion z-motion amplitude is quickly damped by ion-neutral collisions in the presence of a high applied trapping d.c. voltage (e.g., +10 V). The radius of the ion cloud continues to increase due to collision-induced magnetron radius expansion. For ions initially formed on the z axis, collisions of (suprathermal) ions of high z-oscillation amplitude reduce the ion z velocity and accordingly increase the radial ion velocity (and thus increase the magnetron radius, since the cyclotron orbit remains tangent to the z axis). Moreover, when the number of trapped ions is large, space charge repulsions push ions radially outward and also increase the average magnetron radius. In general, any process that decreases the kinetic energy of a trapped ion tends to reduce the z-oscillation amplitude (since ion potential energy decreases as the ion moves axially to the center of the trap) and increase the

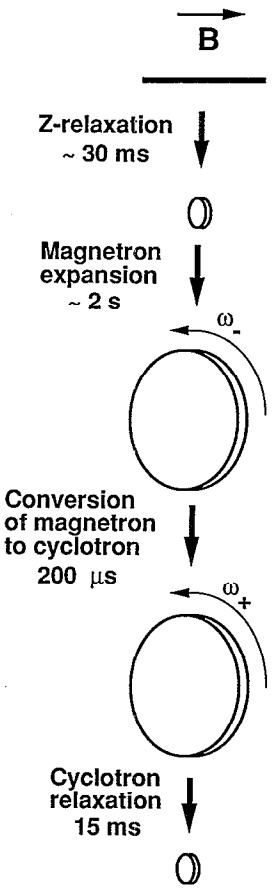

FIG. 2. A schematic illustration of pulsed-mode conversion, cooling, and axialization processes. Proceeding from top to bottom in the diagram, an electron beam creates ions distributed along the z axis in the source trap with small cyclotron and magnetron radii. The rod-shaped ion distribution relaxes in the z direction toward the center of the trap in a few tens of milliseconds at 2×10^{-5} Torr chamber pressure. Subsequent magnetron radius expansion effectively prevents ion transfer through the narrow conductance limit (2 mm diam.) to the analyzer trap. An azimuthal quadrupolar excitation pulse converts magnetron motion into cyclotron motion, without changing the overall radius of the ion cloud. However, the slow magnetron rotational angular velocity ω_- is replaced by the much faster cyclotron rotational angular velocity ω_+. Finally, the cyclotron motion is efficiently damped by ion-neutral collisions and the radius of the ion cloud is significantly reduced. Thus, off-axis ions have effectively been "shrink wrapped" into a narrow cylinder along the z axis.

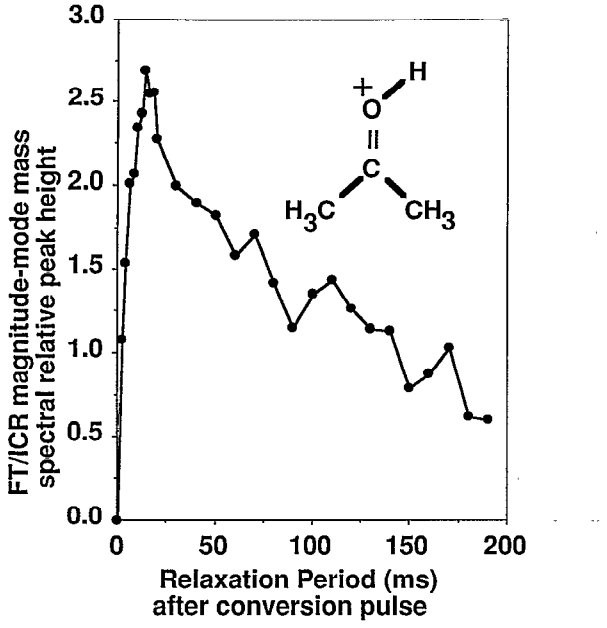

FIG. 3. Evolution of FT/ICR magnitude-mode mass spectral peak height of protonated acetone ions ($m/z=59$) detected in the analyzer trap, as a function of the ion-neutral collisional relaxation period between the magnetron-to-cyclotron conversion pulse and ion transfer from the source to analyzer trap. The initially rapid increase of the signal is due to the collision-induced collapse of the ion cyclotron orbital radius (see Fig. 2). Once ions have relaxed back to the z axis (after $\sim$15 ms in this case), the slow expansion of the magnetron radius eventually reduces the number of ions whose magnetron radius is less than the radius of the conductance limit between source and analyzer traps.

magnetron radius (since ion potential energy decreases with increasing magnetron radius).

The conversion π pulse then converts magnetron motion into cyclotron motion. The slow magnetron rotation (at frequency ω_-) is replaced by a much faster cyclotron orbital rotation (at frequency ω_+). Note that the postexcitation cyclotron orbital radius is the same as the preexcitation magnetron radius, i.e., the overall radius of the ion motion is unchanged [see Eq. (22)]. Following the π pulse, collisions of heavy ions with light neutrals effectively damp the cyclotron orbital motion down to a small cyclotron orbit centered on the z axis.[3] This process effectively "shrink wraps" an ion cloud by squeezing ions initially distributed throughout the ion trap into a compact cylindrical ion distribution centered on the z axis.

Figure 3 shows the FT/ICR magnitude-mode mass spectral relative peak height for protonated acetone ions in the source ion trap as a function of the relaxation period between the end of the conversion π pulse and ion transfer to the analyzer ion trap. At a total pressure greater than 2×10^{-5} Torr, protonated acetone ions ($m/z=59$) undergo several hundred collisions per second, leading to a rapid increase in ion magnetron radius. After a 2.5 s relaxation period, no signal is observed. The radial expansion of the the ion cloud prevents subsequent transfer of those ions from the source trap (where they were created) to the analyzer trap because the conductance limit between the two traps is smaller then the average ICR magnetron radius.

However, application of a short (200 μs, 106 $V_{(p-p)}$) pulse at the combination frequency $\omega_c=\omega_++\omega_-$ of the protonated acetone ions completely converts the magnetron motion to cyclotron motion. During the subsequent relaxation period, the ions lose cyclotron kinetic energy due to collisions with the argon buffer gas. The radius of the ion cloud is reduced at the same rate as the cyclotron damping factor $(\xi\omega_+)/(\omega_+-\omega_-)$. After $\sim$15 ms most of the ions have relaxed back to the z axis and are available for transfer through the conductance limit to the analyzer trap. Of course, the same ion-neutral collisions which reduce the ion cyclotron kinetic energy also lead to expansion in the magnetron radius, but at a rate $(\xi\omega_-)/(\omega_+-\omega_-)$ much smaller than the rate of decrease of the cyclotron radius[13] because the magnetron frequency ω_- is much smaller than the cyclotron orbital frequency ω_+.

Broadband cooling and axialization

To this point, we have succeeded in producing a complete magnetron-to-cyclotron motion conversion for ions of a single mass-to-charge ratio by use of a resonant π pulse. More generally, we would like to be able to produce magnetron-to-cyclotron conversion for ions having a specified range of mass-to-charge ratios, and thus a corresponding range of cyclotron frequencies. In prior work,[22] the properties of Eq. (19) were examined in detail and an algorithm for generating optimally selective and uniform-magnitude broadband excitation was proposed. For example, the generation of a 90° NMR "notch" pulsed excitation was demonstrated. Unfortunately, there is to date no perfect recipe in NMR for generating an excitation waveform which produces complete inversion over a specified frequency band with zero excitation magnitude at other frequencies. Considerable progress has been made by use of optimization procedures to produce an optimal inversion pulse.[23] The hyperbolic secant pulse, which produces well-behaved inversion over a specified frequency range, is the only one whose response can be expressed analytically.[24] Various other pulsed excitation waveforms for population inversion are also available.[25] Finally, the conversion from pure magnetron to pure cyclotron motion is independent of the initial magnetron phase, just as the effectiveness of a 180° pulse in NMR is independent of the initial phase of the magnetization (i.e., if the initial xy magnetization has zero amplitude, its phase is immaterial).

Fortunately, broadband magnetron-to-cyclotron conversion may be achieved in yet another way by analogy to adiabatic rapid passage in NMR.[18] For example, the quadrupolar irradiation frequency ω in Eq. (23) may be swept at a constant rate from a value above the highest ω_c to below the lowest ω_c in the mass-to-charge ratio range of interest. By analogy to NMR, the adiabatic passage condition for magnetron-to-cyclotron conversion is that

$$\frac{d\omega}{dt}\ll\Omega_0 . \tag{24}$$

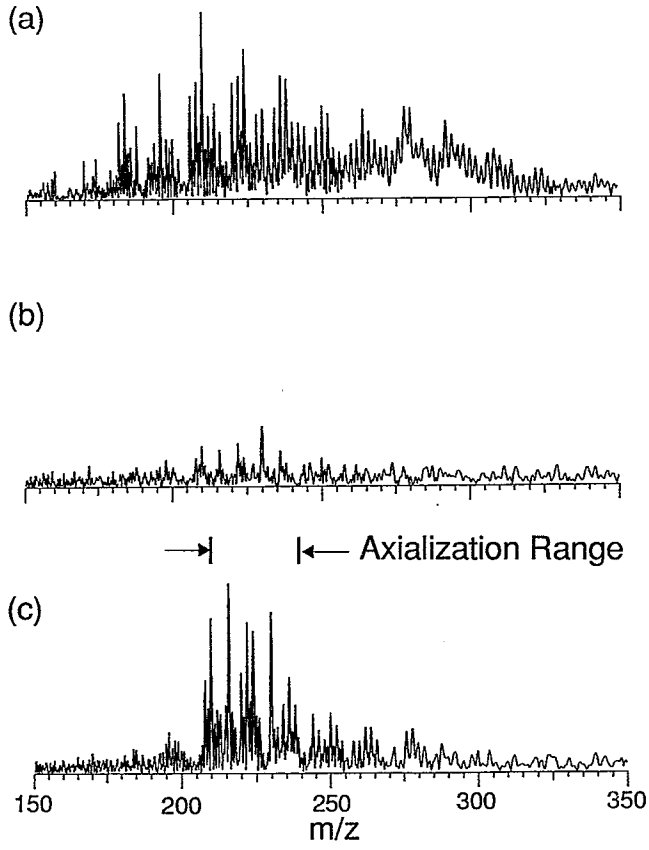

FIG. 4. Broadband cooling and axialization of ions having a wide range of mass-to-charge ratio. (a) Ions produced by electron ionization of a gaseous crude oil distillate sample are transferred to the analyzer immediately after the ionization event; ions over the full m/z range are observed. (b) The same as in (a), but with 0.75 s relaxation period before transfer of ions to the analyzer trap; most ions have magnetron radii too large to pass through the conductance limit aperture. (c) Ions with $210 \leqslant m/z \leqslant 240$ are brought back to the z axis by pulsed quadrupolar frequency-sweep excitation followed by a delay of 20 ms to allow for cooling of cyclotron motion (see the text).

Adiabatic passage is not restricted to frequency-sweep excitation; a general approach for generating an adiabatic rapid passage inversion has been proposed by Pines and co-workers for NMR.[26]

Figure 4 shows the result of a broadband axialization experiment carried out at an argon buffer gas pressure of 10^{-4} Torr, and a crude oil distillate sample at a partial pressure of $\sim 5 \times 10^{-8}$ Torr. If ions are transferred to the analyzer immediately after the ionization event, as shown in Fig. 4(a) the original ion distribution ranging from $150 < m/z < 350$ is observed. A delay of 750 ms between ionization and ion transfer [Fig. 4(b)] results in near-total loss of ion signal due to ion magnetron radius expansion in the source trap. However, ions having a specified range of mass-to-charge ratios may be brought back to the z axis by application of a broadband conversion pulse and the subsequent cooling of cyclotron motion, as shown in Fig. 4(c). Specifically, a quadrupolar frequency sweep (2 ms duration, 106 $V_{(p-p)}$ amplitude, whose start and end frequencies correspond to the unshifted ion cyclotron orbital frequencies ω_c of $m/z=240$ and 210, respectively) effectively converts the magnetron to cyclotron motion over the irradiated m/z range. A relaxation period of 20 ms between ionization and ion transfer was sufficient to provide for cooling of the cyclotron motion. Most of the ions in the selected m/z range are axialized and detected after transfer to the analyzer trap. Finally, Fig. 4(c) also shows that some ions with m/z values outside the irradiated conversion range are partially axialized, in part because the adiabatic condition is not satisfied near the frequency limits of the quadrupolar frequency sweep, and in part because of space charge and nonfrictional damping effects.

CONCLUSION AND SUGGESTED FUTURE DIRECTIONS

Axialization of ions of a single mass-to-charge ratio by use of single-frequency resonant quadrupolar excitation to convert magnetron to cyclotron motion, combined with collisional cooling of the cyclotron motion has previously been demonstrated.[10–12] In this paper, we first extend the homology[27] between ICR and NMR spectroscopy by showing that the Bloch-equation formalism for a two-level system applies to the magnetron-to-cyclotron conversion process in ICR. Then, by analogy to adiabatic rapid passage in NMR, we are immediately able to extend the broadband excitation to produce axialization of ions having an arbitrary range of mass-to-charge ratios. This important extension dramatically increases the potential applications of the experiment. For example, ions of arbitrary mass-to-charge ratios may be trapped for an extended period at high pressure, to provide for up to 10^6 ion-neutral collisions, a critical capability for vibrational and rotational relaxation of internally excited ions. Moreover, ions of a wide range of mass-to-charge ratios, formed off axis (either directly or by any of several fragmentation processes), may be brought back to the z axis for efficient ICR excitation and detection.

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