Broadband axialization in an ion cyclotron resonance ion trap

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A novel broadband ion axialization method has been developed for Fourier transform ion cyclotron resonance mass spectrometry based on Penning trapping of ions. Ions of arbitrary mass-to-charge ratio range(s) may be driven to the center of the trap (axialization) by azimuthal quadrupolar irradiation with repeated low-amplitude stored-wave-form inverse Fourier transform excitations in the presence of a buffer gas. We demonstrate highly mass-selective axialization and subsequent high-resolution Fourier transform ion cyclotron resonance detection of ions spanning a mass-to-charge ratio range of 500.

I. INTRODUCTION

Ions are spatially confined in an ion cyclotron resonance or a Penning ion trap by a strong uniform static magnetic field combined with an axial quadrupolar electrostatic potential, providing a basis for Fourier transform ion cyclotron resonance [FT-ICR] mass spectrometry, a powerful analytical tool for mass analysis.[1] Ion motions in the combined magnetic field and quadrupolar trapping potential may be analyzed into three independent harmonic motions, namely cyclotron, magnetron, and axial motions.[2] FT-ICR determination of ion mass-to-charge ratio is based on measurement of ion cyclotron frequency, which is inversely proportional to ion mass-to-charge ratio, m/z. Optimally, ions should possess near-zero initial velocity and be located at or near the center of the trap. However, ions generated in (or injected into) such a trap may have significant translational energy and/or have nonzero magnetron radius (i.e., off-axis cyclotron orbit center).

It is well known that at high neutral gas pressure, initial cyclotron or axial motional amplitude is quickly reduced by the cooling effect of ion-neutral collisions, because high amplitude cyclotron or axial motion corresponds to high energy partitioned into those modes. In contrast, ion-neutral collisions act to increase the ion magnetron orbital radius, because a large magnetron radius corresponds to a lower magnetron energy (mainly potential energy). Thus, ions are eventually lost radially from the trap by collision-induced magnetron orbit expansion after a prolonged trapping period. The magnetron expansion problem was first addressed by Wineland and Dehmelt,[3,4] who developed a "sideband cooling" technique in which magnetron motion is converted to axial motion, and the axial motion is cooled by coupling to a resistive circuit. Similarly, reduction in magnetron radius may be achieved by converting magnetron motion to cyclotron motion with simultaneous resistive damping of the cyclotron motion.[2] Magnetron-to-cyclotron conversion is achieved by azimuthal quadrupolar resonant excitation at the unperturbed ion cyclotron frequency, ω_c, of the ions. Once

the ion magnetron motion has been completely converted into cyclotron motion, the cyclotron motion may be cooled effectively by ion-neutral collisions. Whereas the resistive cooling method is useful for cooling of light ions or electrons, collisional damping by ion-neutral collisions is a more effective way to cool heavy ions of a single m/z ratio in a Penning trap.[5]

Axialization by azimuthal quadrupolar excitation and collisional cooling—We have adapted the azimuthal quadrupolar resonant excitation/collisional cooling method (henceforth denoted as "axialization") to a dual-trap FT-ICR mass spectrometer.[6] Ions of a given m/z value may be axialized to the center of the source half of the dual-trap at a high buffer gas pressure and then transferred to the analyzer half of the dual-trap for high-resolution detection at much lower pressure. We also demonstrated simultaneous axialization of ions of two different m/z ratio by applying a continuous-wave excitation with Fourier components at the two respective ion cyclotron frequencies.

Axialization of ions over a wide m/z range has been analyzed theoretically, by the close formal analogy between the ion response to azimuthal quadrupolar excitation and the Bloch equation description of the response of a system of spin one-half particles to dipolar magnetic excitation.[7] For example, conversion from pure magnetron to pure cyclotron motion is equivalent to magnetization inversion (180° pulse) in a two-level spin system. We may therefore adapt the excitation methods[8] developed for inversion of a two-level spin systems (shaped-pulses, adiabatic rapid passage, or low "tip-angle") for axialization of ions in FT-ICR mass spectrometry. Of these, adiabatic passage is suitable for nonselective broadband excitation, but is relatively nonselective because of the short excitation period. Moreover, shaped pulses to produce highly selective broadband excitation are not fully understood analytically and no single shaped-pulse method is widely applicable. In ICR, there is the additional problem that the quadrupolar excitation potential is far from ideal except near the trap center. For all of these reasons, high-amplitude azimuthal quadrupolar excitation has not so far been successful in producing highly selective magnetron-to-cyclotron conversion over a wide m/z range.

Suppose that ions have near-zero initial cyclotron and

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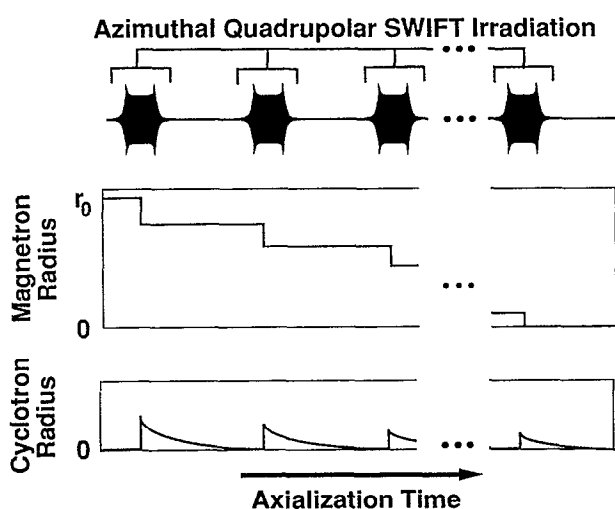
Azimuthal Quadrupolar SWIFT Irradiation

FIG. 1. Schematic representation of a series of identical azimuthal quadrupolar SWIFT excitations (top), and their effect (in the presence of ion-neutral collisions) on ion magnetron radius (middle) and ion cyclotron radius (bottom). Although all SWIFT pulses are identical, their effect decreases as the magnetron radius decreases, because the excitation electric field strength is proportional to radial distance from the trap central z-axis. After each partial magnetron-to-cyclotron conversion, a sufficiently long period is provided to allow the cyclotron motion to relax completely.
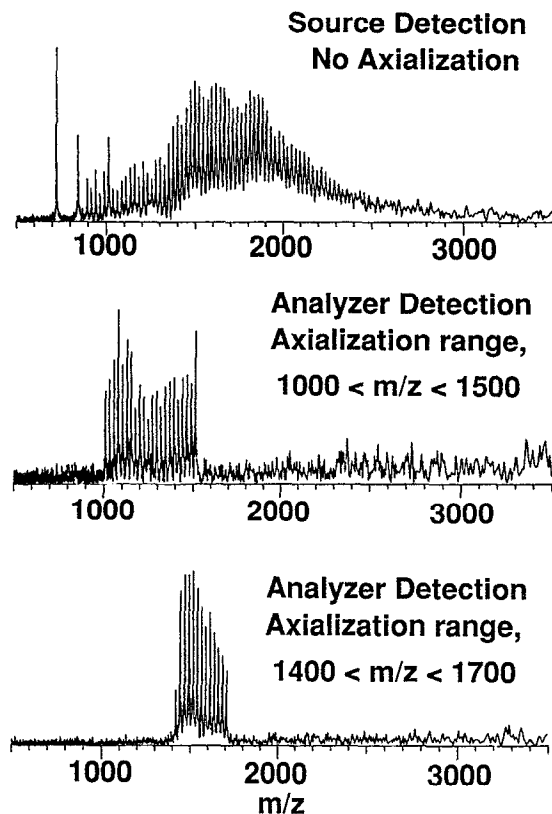

FIG. 2. Broadband FT-ICR mass spectrum of laser-desorbed fullerene anions detected in the source half of a dual trap without prior axialization (top) or following axialization and transfer to the analyzer half of the dual trap (middle, bottom). Beginning 2 s after ion formation, repeated azimuthal quadrupole SWIFT excitation was applied to the source trap for 20 s to axialize ions of $1,000 \leqslant m/z \leqslant 1,500$ (middle) or $1,400 \leqslant m/z \leqslant 1,700$ (bottom).

axial motional amplitudes, as from collisional cooling before any axialization procedure. If the azimuthal quadrupolar excitation is sufficiently low in amplitude, then the corresponding magnetron-to-cyclotron conversion process is linear, just as magnetic resonance low-amplitude excitation is linear in the limit of sufficiently small ($\sin \theta \approx \theta$) "tip-angle." We therefore apply a train of low-amplitude successive identical stored-wave-form inverse Fourier transform (SWIFT)[9,10] excitations (Fig. 1, top), in azimuthal quadrupolar mode, to ions in the presence of a buffer gas. The stored wave form is generated by inverse Fourier transform of a desired magnitude-mode excitation spectrum with appropriate phase modulation.[11,12] Each SWIFT irradiation converts a fraction of the magnetron motional amplitude into cyclotron motional amplitude (Fig. 1, middle); during the interval between SWIFT excitations, the cyclotron motion quickly damps to near-zero radius (Fig. 1, bottom), and the magnetron radius expands only slightly.[13] The process is then repeated, thereby successively reducing the magnetron radius stepwise to zero, and leaving the ions well-localized near the center of the trap. Because the magnetron radius is reduced by only a few percent by any one SWIFT irradiation, the azimuthal quadrupolar excitation process becomes linear,[14] justifying the use of SWIFT excitation.[15,16]

II. EXPERIMENT

Detailed conditions for ion axialization in laser desorption FT-ICR experiments are given elsewhere.[17] Briefly, we use a commercial FT-ICR mass spectrometer, operating at a magnetic field of 3.0 tesla with two adjoining cubic traps separated by a narrow circular (2 mm diam) conduction

limit. Ions are formed by single-shot ~10 ns irradiation at ~30° incident angle of a solid sample area of ~0.2 mm² with unseparated fundamental and second harmonic components from a Nd:YAG laser.[18] A fullerene sample was dissolved in toluene and applied as a thin film[19] on the stainless steel probe tip. Argon collision gas was admitted into the source chamber of the mass spectrometer through a leak valve. Pressure was maintained at 1.2×10^{-7} Torr in the source and $< 0.1 \times 10^{-8}$ Torr in the analyzer chamber.

After ion formation by laser desorption, a 1 s delay is provided to allow the axial and cyclotron motions of ions in the source trap to cool. Azimuthal quadrupolar excitation wave forms were generated from a rectangular frequency domain magnitude profile covering the range of unperturbed cyclotron frequencies ($\omega_c = qB/m$ in SI units), of the ions of interest. SWIFT excitation (1 V_{p-p} for 16.38 ms) from a homebuilt SWIFT module[9] was applied repeatedly (Fig. 1, top) at intervals of 0.39 s for 20 s to axialize the irradiated ions. After axialization and cooling, the conductance limit voltage was lowered to zero for 313.2 μs (Fig. 2, middle) or 342.1 μs (Fig. 2, bottom and Fig. 3) to allow for ion transfer to the analyzer trap; the conductance limit voltage was then reset to the original trapping potential (1.5 V). Ions were
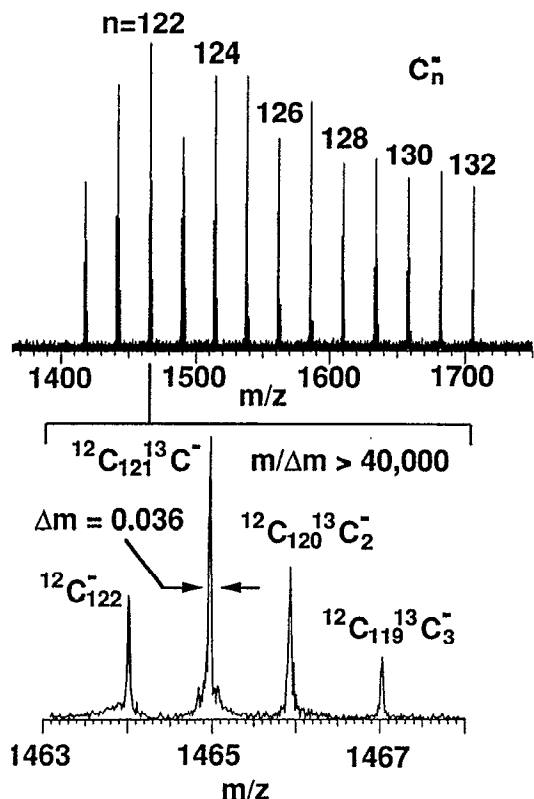
FIG. 3. FT-ICR broadband high-resolution mass spectrum (top) of axialized ions, $1,400 \leqslant m/z \leqslant 1,700$ transferred to the analyzer half of a dual trap (see Fig. 2, bottom), where the pressure, $<0.1 \times 10^{-8}$ Torr, is almost two orders of magnitude less than that in the source trap. The bottom trace show the scale-expanded region for C_{122}^-. The already-high mass resolving power, $m/\Delta m \approx 40,000$, may be further improved by correcting for frequency drift during detection.[24]

$z \leqslant 1,700$ axialized and transferring from the source trap as in Fig. 2 (bottom). Note that a mass resolving power of $\sim$40 000 is achieved for singly-charged ions throughout a 300 u mass range.

With the present newly developed broadband ion axialization technique, it is now possible to trap and selectively isolate ions of arbitrary m/z range(s) at high buffer gas pressure. In this way, ions with high initial translational and internal energy may be efficiently cooled by ion neutral collisions, and centered in a compact ion packet near the center of the trap for subsequent axial injection to another trap for high-resolution detection. Moreover, the SWIFT excitation method provides for axialization with high mass selectivity over multiple m/z tailored windows. Applications for the present broadband axialization technique include: improved ICR peak shape and detection sensitivity (factor of 100 in some cases);[17] improved mass resolving power (up to factor of 500);[17] improved ion remeasurement efficiency (up to 99%) for additional increase in signal-to-noise ratio and/or multiple experiments with a single trapped-ion packet;[23] extended trapping period to allow for thousands of ion-neutral collisions to release excess ion internal electronic or vibrational excitation energy;[6] improved transfer efficiency to move ions through a narrow conductance limit;[17] and reduced z-ejection from excitation at $2\omega_z$ and $\omega_+ \pm 2\omega_z$.

detected in the analyzer trap with standard FT-ICR dipolar excitation/detection procedures.[20]

III. RESULTS AND DISCUSSION

Figure 2 (top) shows that abundant laser desorbed/ionized fullerene anions spanning a m/z range from 720 (C_{60}^-) to $\sim$2800 (C_{230}^-) may be trapped and detected in the source trap. The present multiple low-amplitude SWIFT azimuthal quadrupolar excitation method clearly succeeds in selective axialization (for subsequent source-to-analyzer transfer and standard dipole detection) of ions from $1,000 \leqslant m/z \leqslant 1,500$ (Fig. 2, middle) or $1,400 \leqslant m/z \leqslant 1,700$ (Fig. 2, bottom) from the original fullerene anion mixture. The axialization is uniform, as evident from the agreement between the relative ion abundances detected without (Fig. 2, top) or following (Fig. 2, middle or bottom) azimuthal quadrupolar multiple-SWIFT excitation. (Because ion transfer from source to analyzer traps is itself inherently a mass-selective process,[21,22] we chose a transfer period designed for optimal transfer of ions at the middle of the axialized m/z range.)

Figure 3 demonstrates broadband high-resolution detection in the analyzer trap of fullerene anions of $1,400 \leqslant m/$

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