Effect of Frequency Sweep Direction on Motion of Excited Ions in Fourier Transform Ion Cyclotron Resonance Cells

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Ion motion during frequency sweep excitation was computer simulated to study the effect of the direction of frequency sweep on the z motion of ions in a cylindrical Fourier transform ion cyclotron resonance (FT-ICR) cell. It is shown that the z motion is more forcefully excited by up-sweep than by down-sweep; thus at large amplitudes ions are more easily ejected to the trapping electrodes by up-sweep and larger cyclotron orbits can be achieved by down-sweep. This effect was confirmed by experiment and the results are favorably compared with the calculations. From these results it is concluded that downward sweeping is advantageous for ion detection and upward sweeping is preferable for ion ejection. The simulations clearly explain the effect of the direction of frequency sweep by visualizing the directions of the forces that ions experience immediately after the excitation of their cyclotron motion. It was demonstrated by experiment that the z ejection can be reduced by applying a phase-adjusted ac potential to the trapping electrodes. (*J Am Soc Mass Spectrom* 1992, 3, 847–852)

In Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometers ions are confined in a cell by static electric and magnetic fields and coherently excited to large circular orbits by an rf electric field with their cyclotron frequencies. In FT-ICR spectrometry the excitation is performed for three purposes: First, to detect ions by amplifying the image current induced at detection electrodes of the cell [1]; second, to remove undesired ions from the cell by accelerating them to the boundary of the cell where they are neutralized and lost [2]; third, to increase the kinetic energy of selected ions to carry out collision-induced dissociation experiments [3].

When ions with various mass-to-charge ratios are confined in a cell, their cyclotron frequencies are distributed over a wide frequency range and to execute multichannel detection all the ions must be simultaneously excited. Several different waveforms have been developed for broadband excitation, including frequency sweep ("chirp") [4], stored waveform inverse Fourier transform [5] and impulse [6]. Among others the most commonly used is the frequency sweep. With this waveform, excitation can be performed in two ways: by sweeping the frequency either from low to high (up-sweep) or from high to low (down-sweep). In

this regard, a problem has long been recognized: the direction of frequency sweep affects the FT-ICR signal detection. Rempel et al. [7] have observed that ion image current flows at the third harmonic of the observed cyclotron frequency when the sweep starts from a low frequency and sweeps up, but such current is not observed when the direction of the sweep is reversed. They suggested that the effect is caused by the energy transfer between the orbital motion of excited ions and nonuniform antenna fields in FT-ICR cells. However, we have observed that at frequencies even lower than the third harmonic, higher signal intensity is usually obtained by down-sweeping than by up-sweeping. This suggests that there must be another effect of the direction of frequency sweep on the FT-ICR signal.

In subsequent studies [8–12] it has been made clear that during excitation of the cyclotron motion of ions, by an rf-electric field, the momentum is also transferred to the z motion and the ions are ejected to the trapping electrodes. In particular, Kofel et al. [9] have solved the equation of ion motion by taking into account the coupling between the cyclotron motion and the z motion. Incorporating the terms up to the fourth and third orders in the expansions of the dc and the rf electric fields, respectively, they calculated ICR orbital radii as a function of the frequency and amplitude of a single-frequency excitation pulse. By comparison of computed and observed ICR signal intensities they concluded that during a frequency sweep, if the excita-

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tion frequency is higher than the cyclotron frequency f_c , the z motion is excited, and if the excitation frequency is lower than f_c , the z motion is damped. Van der Hart and van de Guchte [11, 12] have calculated numerical solutions of the equation of motion for an ion in a cubic cell and shown that excitation of the z motion occurs by irradiation at twice the trapping frequency $2f_t$ and $f_c + 2f_t$ but does not take place at $f_c - 2f_t$.

In the present paper ion trajectories during frequency sweep excitation were investigated by computer simulation based on the exact potential formula for a cylindrical cell used in this laboratory, and the effect of the direction of frequency sweep on the z motion is successfully explained. Comparison is made between the simulation and the experimental results on the ion signal intensity (or the final ICR orbital radius) as a function of the amplitude of excitation waveform and a qualitative agreement is obtained. Finally, a method for preventing the z ejection of ions is proposed. It is based on the principle that the z motion can be damped by applying a phase-adjusted ac potential to the trapping electrodes. The effectiveness of the method was proved by experiment.

Computational

Numerical Solution of the Equation of Motion

An exact formula for the potential in a cylindrical cell during excitation has been presented elsewhere in the form of a series expansion [9]. The boundary conditions employed in the present study are shown in Figure 1. The origins of the cylindrical and Cartesian coordinate systems are at the center of the cell. The cell has a radius a . The two trapping electrodes are located at $z = \pm c/2$ and V_t and $\pm V_e$ are the potentials applied to the trapping and the excitation electrodes, respectively.

Figure 1. Schematic drawing of the cylindrical FT-ICR cell. The Cartesian and cylindrical coordinate systems are used in the computations. The origins of the coordinate systems are taken at the center of the cell. Potentials on the various electrodes are indicated.

Electric field components were derived by differentiating the exact potential formula for the cell used in our laboratory (with $a = 0.015$ m and $c = 0.03$ m). In the calculation, the double summation was stopped when the next contribution became less than 0.0001 V/m.

The Lorentz equation of motion for an ion of m/z 132 in a collision-free system was numerically solved with an IBM 6100 workstation using the fourth-order Runge-Kutta algorithm. The program was run at a step size of 1 ns. The magnetic field components were obtained by spline interpolation on the basis of the field map supplied by Oxford Instruments Ltd., who built our superconducting magnet system.

Initial Positions and Velocities of Ions

The motion of ions trapped in an FT-ICR cell is a superposition of three dominant modes: cyclotron motion, magnetron motion (drift motion), and z motion (trapping oscillation). Although the z components of the initial position and velocity of the ions affect both the amplitude and the frequency of the z motion, the initial values themselves are not essential for comparison between the up- and down-sweepings. Thus we chose initial values of z and v_z as $z = c/2 = 0.015$ m and $v_z = 148.5$ m/s (thermal velocity at 350 K) for all calculations. Figure 2 illustrates variables designating the position and velocity of an ion in the x - y plane. An initial cyclotron radius R_c of 6.0×10^{-5} m was determined from the thermal velocity of an ion ($v_{xy} = 210.0$ m/s) at 350 K and a magnetron radius R_m of 2.0×10^{-3} m was selected from the examination of magnetron frequency in refs 13 and 14. In our preliminary calculations it turned out that the initial values of α hardly affect the calculations, whereas the initial values of β significantly alter the results. We therefore fixed α at 0° and repeated the calculations for sixteen different initial values of β ($\beta = 22.5^\circ \times n$ for $n =$

Figure 2. Variables denoting the position and velocity of a positive ion in the plane perpendicular to the cell axis (x - y plane); R_c and R_m are the cyclotron radius and the magnetron radius, respectively.

0, 1, 2, ..., 16) under the same conditions of excitation field.

Experimental

All experiments were carried out with a home-built FT-ICR mass spectrometer [13] equipped with a superconducting magnet operated at 5 T. A cylindrical cell of 0.015 m radius and 0.03 m length was used. Xe^+ ions were generated by applying a 70-eV electron beam pulse of 0.1 μA for 100 ms to a sample of xenon at a pressure of 1×10^{-7} torr. The pressure was measured with an ANELVA NI-10D ionization gauge and was maintained constant throughout the experiments.

Excitation was achieved by frequency sweep excitation at various amplitudes. The excitation waveforms were generated with a Yokogawa AG1200 arbitrary waveform generator and the output was differentially applied to the excitation electrodes of the cell. The ICR signals were differentially detected, amplified, and fed to an input channel of a Yokogawa DL3120 digital oscilloscope. They were sampled at 2 MHz for 8.192 ms. The digital data with 12-bit resolution were transferred to a NEC PC-9801VX personal computer via an IEEE-488 bus and Fourier transformed to give the magnitude-mode frequency domain spectra. The transformation of a 16,384-point transient was performed after zero filling to 128 K points, yielding about 15 points per peak. The peak heights of m/z 132 ions, which are approximately proportional to the cyclotron radii for the same number of excited ions, were measured at various excitation levels, and compared with the computation results.

Results and Discussion

Figure 3 compares computer-simulated trajectories of an ion of m/z 132 in the upsweep field (a) and the two downsweep fields (b) and (c). The trajectories whose z amplitudes are the largest among a group of sixteen amplitudes resulting from different initial β values were selected and shown in the figures. In Figure 3a, the ion trapped at a trapping voltage of 5 V and a magnetic induction of 5 T is irradiated by upward sweeping from 400 to 800 kHz in 1 ms at an amplitude of 28.5 V (peak to peak). Figure 3b represents the results during the downsweep excitation under the same conditions as those in Figure 3a except for the reverse direction of the frequency sweep. In Figure 3c, the downsweep excitation amplitude is increased to 40 V_{p-p} and other conditions are the same as those in Figure 3b. Comparison of Figure 3a and b clearly shows that an increase in amplitude of the z motion by the downsweep excitation is significantly less than by the upsweep for the same excitation amplitude. Further, as shown in Figure 3c, even at an excitation amplitude of 40 V_{p-p} , the downsweep excitation is still accomplished without ion ejection.

Figure 3. (a) Temporal variation of the x , y , and z coordinates of an m/z 132 ion during upward sweeping from 400 to 800 kHz in 1 ms. The amplitude of the excitation is 28.5 V_{p-p} . The trap voltage V_t is 5 V. (b) Temporal variation of the ion position obtained by downward sweeping. All the conditions are the same as those in (a) except for the direction of the frequency sweep. (c) Temporal variation of the ion position obtained by downward sweeping at an amplitude of 40 V_{p-p} . Other conditions are the same as those in (b).

It is common in FT-ICR mass spectrometry to extend the excitation frequency range to zero. In this regard it has been noted by previous authors that the coupling of the axial and radial modes takes place at twice the trapping frequency, $2f_t$, and the seriousness of the loss of ions by this mechanism has been emphasized [12]. In their studies a fixed frequency burst was typically applied to the excitation plates for several milliseconds to excite ion z motion. In contrast with this, in the case of the frequency sweep excitation, the duration of the excitation near $2f_t$ is too brief with the ordinary experimental conditions [15]. At the sweep rate of 400 kHz/ms that is employed in this study the duration would be at most on the order of 10 μ s even taking into account the poor resolution of the z excitation. In fact our preliminary calculations have shown that the z ejection takes place at a low sweep rate of 20 kHz/ms and an excitation amplitude of $25 V_{p-p}$ by both up- and downsweeping; however, no loss of ions is observed at 400 kHz/ms even at an amplitude of $50 V_{p-p}$.

Shown in Figure 4a are the final cyclotron radii obtained by taking the average of the 16 ions with different initial β values (for ejected ions their radii are counted as zero) at various excitation amplitudes. Except for the excitation amplitude the computational conditions are the same as those in Figure 3a (for upsweep) and b (for downsweep). The maximum final radii are 4.0 mm at $V_e = 28.5 V_{p-p}$ in the upsweep and 5.3 mm at $V_e = 40 V_{p-p}$ in the downsweep. Hence, the downsweep excitation can achieve an approximately 30% larger final cyclotron radius than the upsweep excitation. Figure 4b illustrates the experimentally measured peak heights of $^{132}\text{Xe}^+$ ions obtained by up- and downsweeping for various excitation voltages. Striking similarity between the calculation and the experimental results is observed. In Figure 4b the maximum of the signal intensities by the downsweep is about 80% higher than that by the upsweep. These observations disagree quantitatively with the calculated results because the computer simulation is based on the equation of motion for a single ion in a collision-free system and does not take into account the distribution of ion velocities in the actual cell. From both the computational and the experimental results we conclude that downsweep excitation is advantageous for ICR signal detection over upsweep, but for ion ejection upsweep excitation is preferred.

The above effect of frequency sweep direction can be illustrated by the correlation between the rf potential appearing on the excitation electrodes and the temporal y coordinate of ion. As also noted in ref 8, when the potential is higher than the trapping potential V_t (see the top electrode side in Figure 5), the electric field in the vicinity of the electrode has a z component E_z directed toward the trapping electrodes. On the contrary, when the potential is lower than V_t (see the bottom electrode side in Figure 5), the direc-

Figure 4. (a) Calculated final cyclotron radius of an m/z 132 ion obtained by upward and downward sweeping versus excitation amplitude. The conditions for calculation are the same as those in Figure 3a except for the excitation amplitude. (b) Variation of the experimentally measured peak height of $^{132}\text{Xe}^+$ ions as a function of the excitation rf voltage applied to the excitation electrodes. The trap voltage and the frequency sweep conditions are the same as those in (a).

tion of E_z is reversed toward the center of the cell.

Figure 6a and b is an enlargement near the cyclotron frequency of Figure 3a and b. In addition to the y and z coordinates of the ion trajectories, the figures show plots of the temporal potentials appearing on the top electrode V_{TOP} and the bottom electrode V_{BOT} at the moments when the ions come to the top ($y = Y_{\text{TOP}}$) and the bottom ($y = Y_{\text{BOT}}$) of their cyclotron orbits, respectively. In the case of the upsweep (Figure 6a), after excitation of the cyclotron motion of ions, the phase of the rotating vector of the rf electric field goes ahead of the phase of the cyclotron motion. When the former leads the latter by π , the ions experience forces toward the trapping plates as illustrated in the upper

Figure 5. Peak potentials appearing on the excitation electrodes, lines of electric force, and y and z components of the forces acting on positive ions near the electrodes.

Figure 6. Enlarged plots of y and z coordinates of the temporal ion position of Figure 3a (upsweep) and 3b (downsweep) around the cyclotron frequency (581.67 kHz) and the potentials appearing on the top (V_{TOP} denoted by $\circ$) and the bottom (V_{BOT} denoted by $\times$) excitation electrode, when the ion is at the top and the bottom of its cyclotron orbit, respectively. The y coordinates of the ion at the top ($y = Y_{TOP}$) and the bottom ($y = Y_{BOT}$) are indicated by $\cdots$. Within the dashed lines the excited ion undergoes the outward (a) or the inward (b) force as illustrated in the upper or lower half of Figure 5, respectively.

half of Figure 5. Then at another advancement by π the ions undergo forces toward the center of the cell as shown in the lower half of the figure. After that the ions experience alternately outward and inward forces in every advancement in phase by π . Further, when the rf frequency goes away from the cyclotron frequency, the forces are of shorter duration and the effect of the forces acting on the ions becomes averaged out. In the case of the downsweep (Figure 6b), following the cyclotron resonance of ions, the phase of the rf-electric field vector approaches the phase of the cyclotron motion. Thus the ions undergo first the forces toward the center of the cell and then the forces toward the trapping plates. During this second period the ions can be ejected to the trapping plates, if the amplitude of the rf electric field is large enough. However, the net effect on z ejection is less pronounced with the downsweep because of the difference in the order of the directions of the forces acting on the ions with large cyclotron orbits.

The above results have shown that the excited ions are accelerated in the z direction during a time that is comparable to the period of their trap oscillation. Thus it is most likely that following frequency sweep excitation, the z motion of the excited ions becomes coherent to some extent [16]. We therefore propose a method for restraint of the z ejection. In principle the method consists of differentially applying an ac potential that is $\pi/2$ phase shifted relative to the z motion of ions to the trapping electrodes. Figure 7a and b shows the preliminary results demonstrating the efficacy of the method. Ions were excited by downsweep from 700 to 500 kHz in 0.5 ms at an amplitude of $35 V_{p-p}$. In this condition, about 40% of the maximum ion signal was lost by z ejection as shown in Figure 4b. During the excitation an ac potential was differentially applied to the trapping electrodes in addition to the dc-trap potential, and the frequency, amplitude, and phase angle of the ac potential were systematically changed to search for a maximum in ion signal intensity. In this manner a 45% increase in signal was obtained at a frequency of 24 kHz, which corresponds to the trap oscillation frequency of $^{132}\text{Xe}^+$ ions. Figure 7a illustrates the variation of signal intensity as a function of the frequency of ac-trap potential with amplitude and phase angle fixed. The horizontal dashed line indicates the signal level observed without the ac potential. Figure 7b presents the variation of signal intensity as a function of the phase angle of ac trap potential with frequency and amplitude kept constant. Because the instantaneous phase angle of the z motion of ions is unknown in practice, it is impossible to correlate the phase of the ac potential to that of the z motion directly. Thus the origin of time t of the ac potential function was synchronized with the onset of the frequency sweep excitation waveform. A minimum and a maximum are observed at phase angles that differ by π , indicating that enhancement and restraint of the z ejection take place at these angles.

Figure 7. (a) Variation of $^{132}\text{Xe}^+$ ion signal intensity as a function of the frequency f_{tac} of the ac potential applied to the trapping electrodes. The $^{132}\text{Xe}^+$ signal was obtained by down-sweep excitation from 700 to 500 kHz in 0.5 ms with the amplitude $35 V_{p-p}$. During the excitation the ac potential was differentially applied in addition to the dc trapping potential (i.e., $V_t = \pm V_{tac} \sin(2\pi f_{tac} t + \theta) + V_{tdc}$ for $0 \leq t \leq 0.5$ ms; $t = 0$ is taken at the onset of the frequency sweep). The data were obtained at $\theta = 1.60\pi$, $V_{tac} = 0.28$ V and $V_{tdc} = 5$ V. The horizontal dashed line indicates the signal level observed without the ac trapping potential. (b) $^{132}\text{Xe}^+$ signal intensity versus the phase angle θ at $f_{tac} = 24.0$ kHz. Other conditions are the same as those in (a).

Conclusions

In summary, our computations of ion trajectories during frequency sweep excitation have shown that the z motion is more forcefully excited by up-sweep waveforms than by down-sweep waveforms; thus larger cyclotron orbits can be achieved by the latter than by

the former. The difference between the two directions of frequency sweep has been confirmed by an experiment measuring ICR signal intensity as a function of the rf voltage applied to the excitation electrodes. The results have been compared with the computations and a qualitative agreement was obtained. From both the simulation and the experimental results it can be concluded that down-sweep excitation is advantageous for ion detection and up-sweep excitation is preferable for ion ejection. Furthermore our simulations have clearly illustrated the effect of the direction of frequency sweep by visualizing the phase correlation between the potentials appearing on the excitation electrodes and the temporal y coordinates of ions. Immediately after the excitation of the cyclotron motion of ions there follows a brief period in which the ions constantly undergo forces directed either to the trapping electrodes (for up-sweep) or to the center of the cell (for down-sweep). Finally, a method for damping the z ejection has been proposed. It consists of applying an ac potential to the trapping electrodes. The efficacy of the method has been confirmed by experiment.

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