

Phase Synchronization of an Ion Ensemble by Frequency Sweep Excitation in Fourier Transform Ion Cyclotron Resonance

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The Fourier transform ion cyclotron resonance (FT-ICR) signal is produced by the coherent motion of a population of ions. The ability to produce a well-defined ion packet by excitation of an initially random ion ensemble is a major limiting factor of high mass FT-ICR. Ions must be both resonant and in phase with the applied radio frequency excitation field to be accelerated to radii suitable for detection by FT-ICR. Synchronization of the phase angles of an ensemble of ions occurs by off-resonant acceleration during frequency swept excitation. Results from computer-simulated ion trajectories suggest that phase synchronization of the ion packet prior to resonant excitation results in better spatial definition of the ion ensemble.

INTRODUCTION

The basis for ion cyclotron resonance (ICR) is the periodic circular orbit of an ion in a homogeneous magnetic field (1). The period of the cyclotron orbit corresponds to a specific frequency; thus ion detection by ICR is achieved by relating the frequency of the orbit to the mass of the ion. The FT-ICR signal is produced by accelerating an ion population into a cyclotron packet which induces an image current in the receive plates of the ICR cell (2-4). The performance characteristics associated with FT-ICR (e.g., sensitivity (5), mass resolution (6), mass range (7), and Fellgett advantage (8)) arise from the ability to produce a spatially defined ion packet from an initially random ion ensemble. Spatial definition of the ion packet is defined by a combination of the radial distribution (distribution of kinetic energy in the X - Y plane) and the radial dispersion (angular distribution) (9). In most FT-ICR experiments (performed with electron impact ionization) the radial distribution of the initially formed ions is small and the ions have near-thermal kinetic energies. Consequently, the radial distribution of the ions does not adversely affect ion detection. It is important to note that some ICR experiments (e.g., experiments utilizing methods that involve momentum transfer, such as secondary ion mass spectrometry (SIMS), collisional ionization, or ion injection from an external source (10-12)) are not adequately described by models based on electron impact ionization of a static gas.

Although there has been recent success in the detection of high mass nonpolar organic ions by laser desorption FT-ICR (13), the ion dynamics involved are different than those experienced with other desorption ionization methods (e.g., SIMS (14, 15), ^{252}Cf -PDMS (plasma desorption mass spectrometry) (16), etc.). In the case of laser desorption within the ion cell, a large number of ions and neutrals are produced during the desorption process (17). Ions that are desorbed in this manner are thermalized by ion-neutral interactions (18) and recent results suggest ion-ion interactions also play a role in ion trapping (19). Conversely, ions that are produced by SIMS are initially formed with a relatively large distribution of kinetic energies, and because SIMS experiments are performed by using low primary beam densities, the yield for neutral species is not sufficient for ion-neutral relaxation.

Similarly, ion motion and the absence of ion-neutral relaxation further complicate experiments performed by using an external ion source instrument. Thus, for SIMS and external ion source instruments it is possible that ions are trapped in the ion cell with initially random phase angles and relatively high (1-10 eV) kinetic energies. Because the ability to "drive" ions into a coherent ion packet is inversely related to the ions translational energy (20), ions that are trapped in the ICR cell with significant kinetic energies yield poorly defined ion packets following resonant excitation. The inability to produce coherent motion in a spatially discrete packet of ions results in the loss of both sensitivity and resolution.

The principal factor in the production of a coherent ion packet is the ability to drive an ensemble of ions having initially random velocity vectors (e.g., random phase angles) into coherent motion (i.e., having a narrow angular distribution). Because the final radial distribution of a population of ions is dependent upon how quickly the random ensemble is "driven" into coherent motion (20), ion detection by FT-ICR is a direct result of the phase angle synchronization of the initially random ion population. Phase angle synchronization of the ion ensemble is a result of ion interaction with an electric field. In a typical broad-band FT-ICR experiment, ion excitation is achieved by sweeping a radio frequency (rf) oscillator over a range of frequencies corresponding to the mass range of interest. Individual ions experience a net gain of translational energy as their respective frequencies come into resonance. Although ions only receive a net gain in kinetic energy during resonant excitation, ions experience the electric field force during the entire excitation period. In order to understand the processes of phase angle synchronization of the ion ensemble, the effect of ion interaction with a non-resonant rf electric field must be examined.

The process of phase synchronization on the dimensions of the ion packet following excitation is difficult to evaluate in a simple cubic ICR cell. Ions that are produced as a result of electron impact have kinetic energies corresponding to those of the neutrals prior to ionization. Thus, ions are driven into phase coherence quickly and accelerated as a well-defined ion packet; thus the impact of phase synchronization is negligible. On the other hand, ions that are formed with appreciable kinetic energies are introduced into the cell with undefined velocities and spatial locations. Direct measurements of the spatial dimensions of the ion packet in a simple cubic cell are difficult due to the lack of an unambiguous diagnostic procedure for probing the effect of phase advancement and ion excitation. The objective of this paper is to discuss the process of phase advancement and evaluate the effects of off-resonant acceleration prior to resonant excitation on the formation of a coherent ion packet for detection by FT-ICR.

MONTE CARLO CALCULATIONS

In order to address the effect of phase angle on ion excitation, it was necessary to develop a computer program that allowed user-defined initial ion conditions. Of primary importance was the ability to define the initial phase angle of the ion motion with respect to the applied rf excitation. To

investigate the effect of ion excitation in FT-ICR, an ion trajectory model was developed by Eyler and co-workers (21) based on the motion of charged particles in a magnetic field (22). This program was expanded and modified by Castro and Russell (23) to allow precise control of excitation waveform and initial ion conditions (i.e., ion location, initial phase angle with respect to the applied rf electric field, initial kinetic energy of the ion, etc.). This enhanced program permits systematic evaluation of the effect of ion kinetic energy and phase angle on excitation and the production of the coherent ion packet.

The computer program is based on an analytical solution of the equations of motion for ions accelerated by an applied rf electric field. Only ion motion in the X - Y plane is addressed by the program to allow specific studies of radial motion to be performed. To do this the equations of motion for an ion of a given mass, charge, and velocity in a homogeneous magnetic field were derived for ion excitation in a homogeneous rf electric field. The electric and magnetic forces acting on an ion were calculated based on the ions temporal location in the applied fields. On the basis of the forces acting on the ion at the location, an ion trajectory was calculated. From the trajectory calculation, a new ion location was determined. Following an operator-determined time interval, the computer program iteratively calculates a new ion location and ion trajectory. The frequency of the applied rf electric field was incremented to allow frequency sweep excitation studies.

RESULTS AND DISCUSSION

The original theoretical treatment for resonant excitation in ICR was developed by neglecting the effect of the initial phase angles of the ion population (24-26). However, recent work suggests that the phase angle cannot be neglected for ions having significant radial translational energies (13, 20, 28). Such considerations are consistent with work reported by Eyler (27).

Phase synchronization of an incoherent ion ensemble occurs through the process of phase advancement. For example, an ion that is initially out-of-phase with respect to the applied resonant rf excitation must phase advance into synchronous alignment with the electric field prior to a net gain of translational energy (13, 20, 28). A change in the relative phase angle of an ion in a cyclotron orbit requires a shift in the period of that orbit. Because the cyclotron frequency is related to the mass-to-charge ratio and the magnetic field strength and independent of the translational energy of the ion, acceleration of an ion in a magnetic field (i.e., a change in the ion's translational energy) results in a larger cyclotron radius and not a change in frequency. Conversely, the effective frequency of an ion in a combined electric and magnetic field is a function of the ion's kinetic energy.

The mechanism for both ion excitation and phase advancement is the application of a resonant oscillating electric field. An ion moving in phase with the applied rf is continuously accelerated (acceleration is caused by the synchronous alignment of the ion's motion with the force vectors produced by the rf field) whereas an ion moving out-of-phase ($\gamma \neq 0$) with the applied rf field experiences a synchronous misalignment of the velocity and electric field force vectors (20). As illustrated in Figure 1, the misalignment of an out-of-phase ion with the applied rf electric field creates a net force perpendicular to the ion motion ($F_{E\perp} = qE_{\perp} = qE \sin \gamma$). The frequency shift required to move an out-of-phase ion into synchronous alignment with the applied electric field is achieved by effect of $F_{E\perp}$ on the ion's angular frequency. The perpendicular component of the applied electric field causes a shift in the angular frequency of the ion (i.e., $\omega_{rf} \neq \omega_{ion}$) allowing phase advancement and synchronization of the ion ensemble to occur.

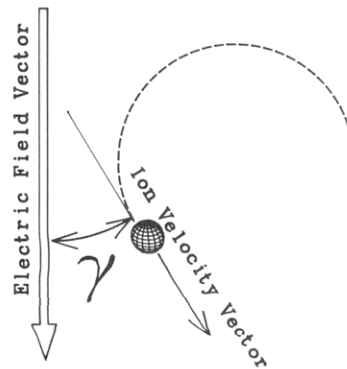


Figure 1. Illustrated is the effect of the misalignment of an out-of-phase ion with the applied rf electric field. The misalignment creates a net force perpendicular to the ion motion ($F_{E\perp} = qE_{\perp} = qE \sin \gamma$) resulting in a frequency shift.

The magnitude of the frequency shift determines how rapidly phase synchronization occurs. Because the magnetic field is velocity dependent, ions having low translational energy experience a strong component of the electric field relative to that of the magnetic field. The perpendicular component of the electric field causes a significant frequency shift and phase advancement occurs rapidly. Conversely, high radial ion velocities increase the force of the magnetic field with respect to the force of the electric field. Under these conditions, the frequency shift induced by the perpendicular component of the rf electric field is reduced (i.e., $\omega_{rf} \approx \omega_{ion}$). Consequently, phase advancement and phase synchronization do not occur instantaneously.

The time required for phase advancement reduces the total amount of translational energy gained during a discrete excitation period. For example, an ion that is initially in-phase with the rf excitation gains translational energy during the entire excitation period (τ_{total}). Conversely, phase advancement occurs over a finite period (τ_{phase}) for an ion that is initially out of phase and the ion gains translational energy during some fraction of the total excite period ($\tau_{total} - \tau_{phase}$). Ions having initially random phases and significant radial velocities therefore yield a significant energy distribution following resonant excitation. An ion ensemble having a distribution of kinetic energies following resonant excitation corresponds to a large radial distribution of the ion packet (i.e., poorly defined spatial dimensions in the X - Y plane).

EFFECT OF MASS AND ENERGY ON PHASE SYNCHRONIZATION

Studies of the effects of mass and energy on ion motion and ion excitation are simplified by Monte Carlo simulations. The computer simulations assume totally homogeneous electric and magnetic field gradients. Ion location is determined by calculating the resultant vectors of the electric and magnetic fields. The effects of mass and energy on phase synchronization are illustrated by observing the effect of rf excitation for an ion which is initially in-phase ($\gamma = 0$) compared to that of an ion which is initially out-of-phase ($\gamma = 180^\circ$). Figure 2A contains a temporal plot of the calculated trajectories for two ions (m/z 500) having thermal kinetic energy and a relative phase angle of 180° . The trajectories result from acceleration of the ions with a resonant, single frequency rf field (900 V/m). Because the initial radial velocity is low, $F_{MAG.} \approx F_{ELEC.}$ phase synchronization of the ion with the rf electric field occurs quickly and the ions are excited as a coherent packet. Conversely, ions that have initial radial velocities corresponding to 3 eV of kinetic energies follow markedly different trajectories (see Figure 2B). The ion that is out-of-phase experiences a continuous misalignment with the electric field resulting in a different trajectory compared to that of an ion which is

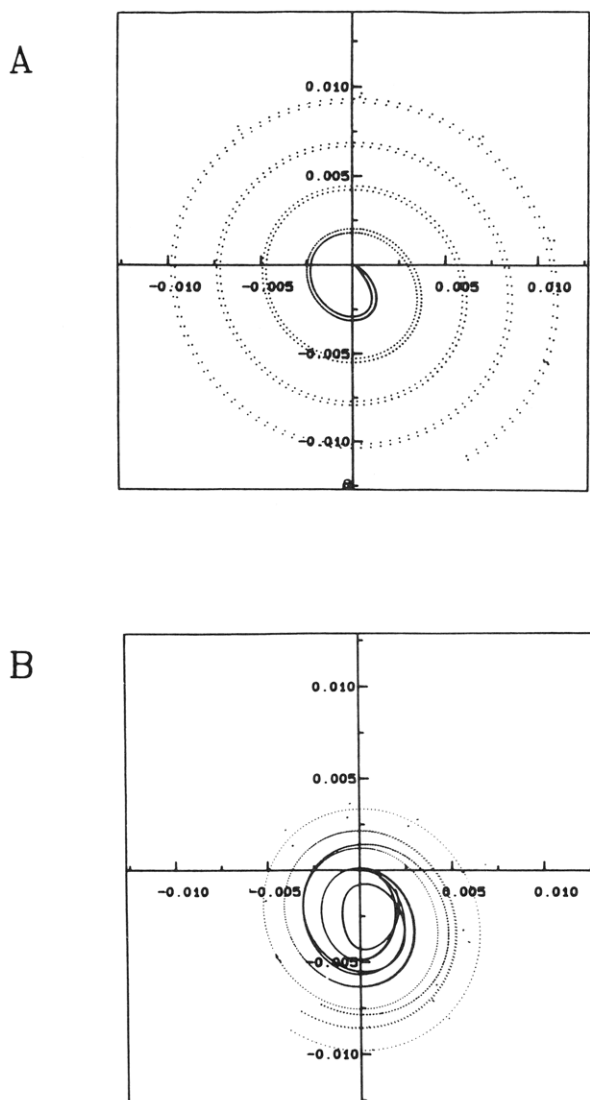


Figure 2. Contained are temporal plots of ion location (axis plotted in cm) from the calculated trajectories in a 3-T magnetic field for two ions (m/z 500) having (A) thermal translational energies and (B) significant translational energies (3 eV) with a relative phase angle of 180° .

initially in phase. The simulations show that instantaneous phase synchronization prior to a net gain of translational energy results in better spatial definition of the ion ensemble following excitation. The spatial distribution of the ion packet following excitation is defined by the relative differences in the temporal locations of the ions comprising the ion ensemble. For example, the ions having well-defined (i.e., coherent) dimensions have negligible differences in their temporal positions relative to the average radius of the ensemble. Such an ion ensemble can be approximated by a rotating monopole (28).

The effect of mass on phase synchronization and the ability to produce a coherent ion packet can be studied by observing the simulated trajectories for two ions having relative phases of 180° ($\gamma = 0$ and 180° relative to the applied rf field). Illustrated in Figure 3A are the trajectories for two ions of m/z 20 accelerated by a resonant rf field. The final orbits (shown as dashed lines) show that at times corresponding to $\gamma = 180^\circ$ (T1) and $\gamma = 0$ (T2), the temporal positions of ion A (initially in phase) and ion B (initially out-of-phase) are separated by a distance that is small with respect to the final dimensions of the orbits. The near identical trajectories for the two ions arise because the shift in the orbit center (illustrated by a solid arrow) and the differences in final radii

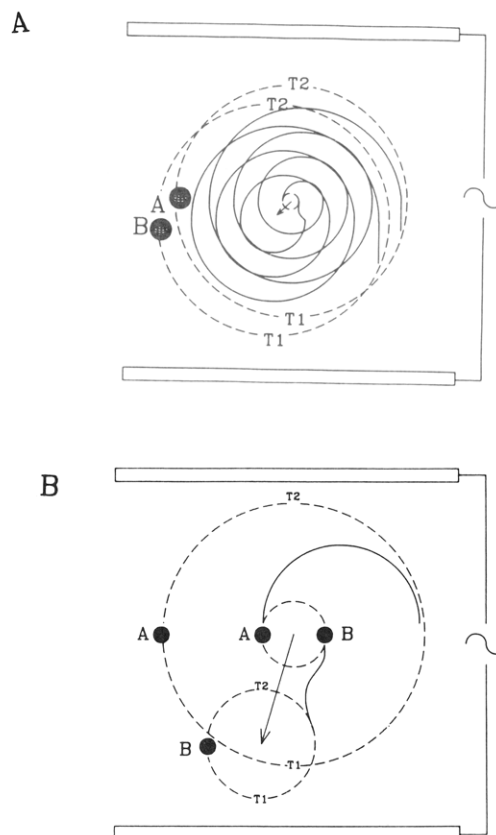


Figure 3. Trajectories for two ions (m/z 20 (A) and m/z 4000 (B)) having a phase relationship of 180° ($\gamma = 0$ and 180° relative to the applied electric field) are illustrated.

are both small relative to the final radius of orbit. Figure 3B contains a similar plot for the trajectories for two ions of m/z 4000. Although the ion initially out-of-phase (B) is driven into phase synchronous motion relative to an in-phase ion (A), there are significant differences in both the final radii and the centers of the cyclotron orbits. At time T1 both ions contribute to the ICR signal. However, because of the spatial differences in cyclotron orbits, the resultant signal from ion B will be reduced at time T2. Therefore, the inability to produce spatial coherence leads to a reduction in the detected signal.

The effect of mass on the magnitude of the center shift and the deviations in relative radii is illustrated in Figure 4. The plots contained in Figure 4 were obtained by comparing the simulated ion trajectories for two ions (in and out of phase with respect to the applied rf field) which have significant initial kinetic energies (3 eV). Ions of a given m/z ratio are accelerated to a final radius that is suitable for detection by FT-ICR (ca. 1 cm). The time required for phase synchronization results in a difference in the energy gained by an ion which was initially in phase and an ion which must undergo phase synchronization prior to gaining energy.

Figure 4A shows the mass dependence for the radial deviation accompanying rf excitation of out-of-phase ions. The mass dependence arises as a result of time required for phase advancement to occur (τ_{phase}). If τ_{phase} is significant relative to the period of a cyclotron orbit, then the time required for phase advancement of an out-of-phase ion increases with mass. It is important to note that the total excitation time (τ_{total}) of the ion ensemble is limited by the time that an in-phase ion can be accelerated prior to ejection from the ICR cell. Because τ_{total} is constant for both in-phase and out-of-phase ions, the differences in the net period of excitation ($\tau_{\text{net}} = \tau_{\text{total}} - \tau_{\text{phase}}$) also increase as a function of the mass. The differences in the radii of high mass ions arise because of the dependence

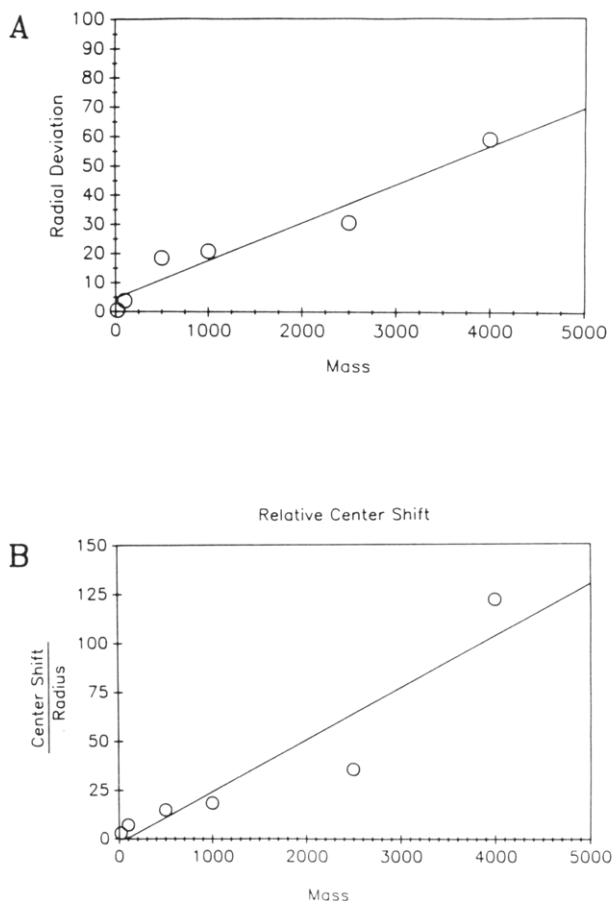


Figure 4. A plot of the effect of increasing mass on (A) the magnitude of the radial deviation (expressed as percent) and (B) on the magnitude of the relative shift in the center of the cyclotron orbit (compared to the final radius of the ensemble) determined for two ions of a given m/z ratio having a phase relationship of 180° . A linear regression of the data from the calculations illustrates the trend.

of the cyclotron radius on τ_{net} . For example, the out-of-phase ion (B) in Figure 3B required a finite time to phase advance (τ_{phase}) which reduces the net period for excitation ($\tau_{\text{total}} - \tau_{\text{phase}}$) compared to that of the in-phase ion (A). Because ion B acquired kinetic energy for a shorter period of time, the final radius of ion B is significantly smaller than that of ion A.

Figure 4B correlates the effect of mass on the magnitude of the center shifts for two ions having a phase relationship of 180° . For ions having the same initial kinetic energies, the resulting shift in the center of the cyclotron radius for the out-of-phase ion is directly dependent on the m/z ratio. The distribution of the ion ensemble arises because the center shift of the out-of-phase ions requires a deflection of the ion's momentum. Because the radius of an ion's curvature in a magnetic field is directly related to its momentum, the magnitude of the resulting center shift increases with mass.

The combined effects of both increasing the deviation of the different radii and relative center shifts result in an inability to produce coherent ion motion for high mass ions having initially significant (ca. 3 eV) kinetic energies and random phases. The plot contained in Figure 5 illustrates the decrease in the degree of coherence which is obtained by resonant acceleration as a function of mass. In this plot the degree of coherence is defined by the relationship described by eq 1. In this relationship, r_{ave} is the average radius achieved by the ion ensemble following excitation and r_{dev} is average deviation of the different ions about that radius. Such a deviation is therefore a function of both the center shift and radial deviation (13, 20, 28).

$$\text{degree of coherence (\%)} = 10^2(r_{\text{ave}} - r_{\text{dev}})/r_{\text{ave}} \quad (1)$$

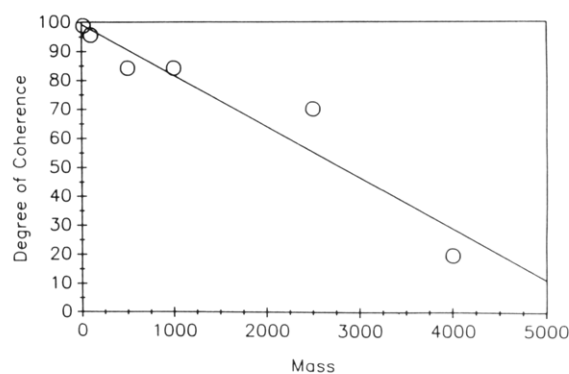


Figure 5. A linear regression of the data obtained from the Monte Carlo plots illustrates the effect of mass on the degree of coherence of the ion ensemble. The data are obtained from the calculated ion trajectories and combine the effects of both the center shift and radial deviation on two ions of a given m/z ratio having a phase relationship of 180° .

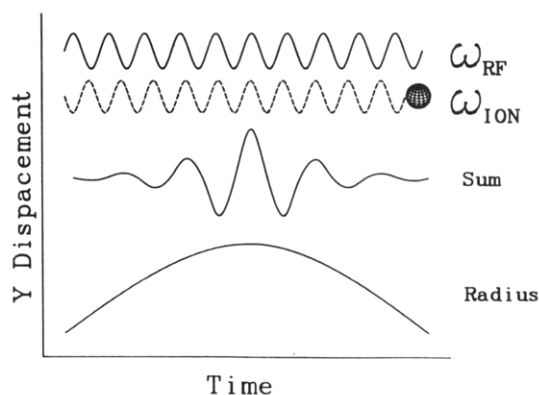


Figure 6. A plot of Y displacement as a function of time is illustrated for the relative position of an ion which is accelerated by a frequency which is discretely different from its cyclotron frequency. The ion moves in- and out-of-phase with respect to the applied electric field. When the ion is in-phase, it will gain translational energy and the associated cyclotron radius will increase. When it is out-of-phase, the misalignment of the electric field force vectors will decelerate the ion resulting in a smaller cyclotron radius.

OFF-RESONANCE EXCITATION AND PHASE SYNCHRONIZATION

The addition of two waveforms of different frequencies results in an interference pattern in time. The pattern of interference (i.e., the beat frequency) arises by the periodic constructive and destructive addition of the two waves. The node of a beat frequency corresponds to a time at which the two waveforms are 180° out of phase, whereas, the maximum amplitude of the beat frequency occurs when the waveforms are in phase. The beat frequency for an ion and an oscillating electric field of different frequency (i.e., off-resonance) is illustrated in Figure 6. The ion moves in and out of phase with respect to the applied rf excitation resulting in ion energy that varies with $\sin^2(t)$ (29). When the ion is in phase with the applied rf excitation, it is accelerated to higher translational energy (i.e., a larger cyclotron radius). During the node of the beat frequency, the ion is decelerated to lower translational energy (i.e., a smaller cyclotron radius). Thus, the radius of cyclotron orbit continuously oscillates as it interacts with the electric field. Because of the oscillation of the beat frequency, ions are continually accelerated (excited and deexcited) with no net gain of kinetic energy.

The translational energy acquired by an ion during frequency sweep excitation has been studied by Marshall and co-workers (30). The instantaneous power absorption is related to the rate that the frequency is swept and the difference between the applied and cyclotron frequencies (13, 20, 28).

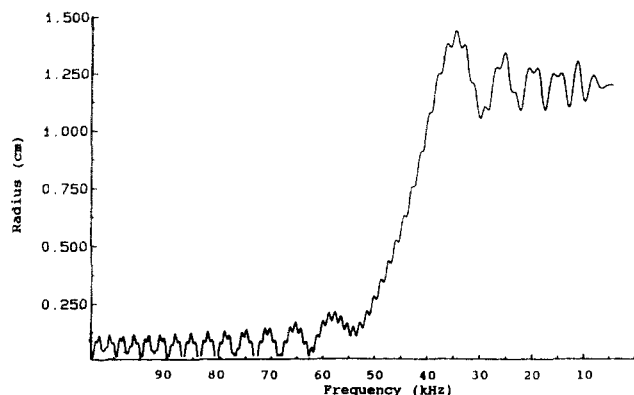


Figure 7. A plot of ion radius (m/z 1000, 3-T B field, 0.01 eV initial kinetic energy) during frequency sweep excitation clearly demonstrates the effect of off-resonant excitation. Ions are constantly accelerated by the applied electric field during the entire excitation period. There is only a net gain of translational energy when $\omega_{\text{applied}} = \omega_c$. This results in a continuous oscillation of the cyclotron radius similar to single frequency off-resonance excitation.

During frequency-sweep excitation of the ion ensemble, ions of all m/z ratios are continuously accelerated and decelerated when $\omega_{\text{applied}} \neq \omega_c$, and a net gain of translational energy only occurs when $\omega_{\text{applied}} = \omega_c$. The oscillation of the cyclotron radius during swept excitation can be observed by numerical solutions to the equations of ion motion (27, 31). Contained in Figure 7 is a plot of cyclotron radius vs applied frequency during swept excitation. The modulation in the cyclotron radius prior to a net gain of energy clearly demonstrates the effect of off-resonance acceleration on ion motion. It is important to note that ions of all m/z ratios are influenced by the electric field, regardless of the applied frequency and that there is no net gain of kinetic energy prior to $\omega_{\text{applied}} = \omega_c$.

Phase synchronization of ions trapped in an FT-ICR cell occurs through interaction with an applied electric field. Because no mechanism exists for moving ions out of phase with respect to the electric field, phase synchronization is *directional*. For example, ions that have the same relative phase angle will experience identical force vectors at any time during the oscillation of the electric field. As long as the forces acting on the two ions are the same, they continue to move coherently. Therefore, an initially random ensemble of ions driven into phase coherent motion continue to move in phase in the absence of collisions.

All ions comprising an ion ensemble interact with the applied rf field during a frequency sweep excitation. Because of the off-resonant interaction of the ion ensemble with the swept frequency, ions are "driven" into phase synchronous motion prior to $\omega_{\text{applied}} = \omega_c$. Ions that are driven into phase during frequency sweep excitation remain in phase. The question we now pose is can off-resonance excitation cause phase synchronization of an ion ensemble prior to resonant acceleration for detection, i.e., result in better spatial distribution of the coherent ion packet.

It is important to realize that frequency sweep excitation affects more than ion energy. In experiments using "chirp" or swept excitation, the interaction of the ion with nonresonant electric fields must be considered. The effect of nonresonant phase synchronization prior to resonant acceleration is illustrated by computer-simulated ion motion. Ion packet definition following swept excitation can be evaluated by varying only the sweep duration prior to resonant acceleration. Off-resonant phase synchronization can be evaluated by monitoring packet dimensions as a function of sweep duration prior to $\omega_{\text{applied}} = \omega_c$.

Figure 8 contains plots of trajectories for m/z 500 ions (initial kinetic energy of 3 eV) resulting from frequency sweep

excitation (1378 V/m, 2.54 cm cell, 3 T) to a final energy of ca. 100 eV. The effect of phase angle and ion velocity is examined by using four ions having phase angles corresponding to $\gamma = 0, 90, 180, 270$. By selection of specific phase angles, it is possible to illustrate the behavior of a random ion ensemble. Figure 8A contains a plot of the temporal ion locations following a swept excitation initiated at a frequency corresponding to m/z 50. That is, ions of m/z 500 interact with the electric field (with no net gain in translational energy) during the swept excitation between m/z 50 and m/z 500. At a sweep rate of 884 Hz/ μ s, ions of m/z 500 interact with the electric field of ca. 1 ms prior to resonant acceleration. The plot of ion location contained in Figure 8D is a result of a frequency sweep initiated at a frequency corresponding to m/z 300. During the abbreviated frequency sweep, ions of m/z 500 interact with the electric field for ca. 0.2 ms prior to a net gain of kinetic energy. These plots illustrate that longer interaction time with the applied electric field results in better definition of the ion packet following excitation.

Contained in Figure 9 is a plot of the effect of sweep duration on the relative dimensions of the ion ensemble. The degree of coherence achieved for four ions ($\gamma = 0, 90, 180, 270$ and 3 eV of kinetic energy) of m/z 500 is determined for different interaction times prior to resonant excitation. From this relationship, it is clear that longer interaction times with the rf electric field prior to resonant excitation results in a better defined ion packet for detection by FT-ICR.

PRACTICAL ASPECTS OF OFF-RESONANCE EXCITATION FOR DETECTION OF HIGH MASS IONS

The high sensitivity and high resolution attributed to FT-ICR arise from the ability to produce a well-defined ion packet by excitation of an initially random ion ensemble. Ions must be both resonant and in-phase with the applied rf excitation field to be accelerated to radii suitable for detection. Ions are driven into phase coherence by interacting with a resonant rf frequency. However, phase angle synchronization of the ion ensemble can also occur by off-resonant acceleration during frequency swept excitation. As illustrated by the data contained in Figures 8 and 9, phase synchronization of the ion packet prior to resonant excitation results in a higher degree of coherence of the detected ion packet.

The spatial distribution of an ion population is affected by the interaction time with the applied electric field. In an FT-ICR ion cell, a high mass ion cannot interact with as many oscillations of the resonant rf electric field as a low mass ion prior to ejection from the ion cell. This limitation reduces the ability to produce a spatially defined packet of high mass ions. The impact of phase synchronization and phase advancement therefore increases with increasing mass and energy. High mass ions injected into the ICR cell (from an external ion source or from a surface bombarded by an energetic particle) with significant translational energies yield a poorly defined ion packet following excitation.

The effect of frequency swept phase synchronization on ion detection has been observed experimentally. Early Cs⁺ desorption experiments showed a dramatic loss of signal when the translationally hot ions were detected in a high-resolution narrow band mode compared to a broad band detection scheme (32). That is, in the narrow-band mode (either direct or heterodyne) off-resonant excitation does not occur. Similar observations have been made for tandem quadrupole/FT-ICR experiments (33). Although detection of high mass ions is possible by broad-band frequency sweep excitation (chirp), the signal is greatly attenuated in the narrow-band mode (i.e., near resonant excitation with reduced interaction time with the electric field). Observations such as these are difficult to quantitate but are consistent with one of the problems (which

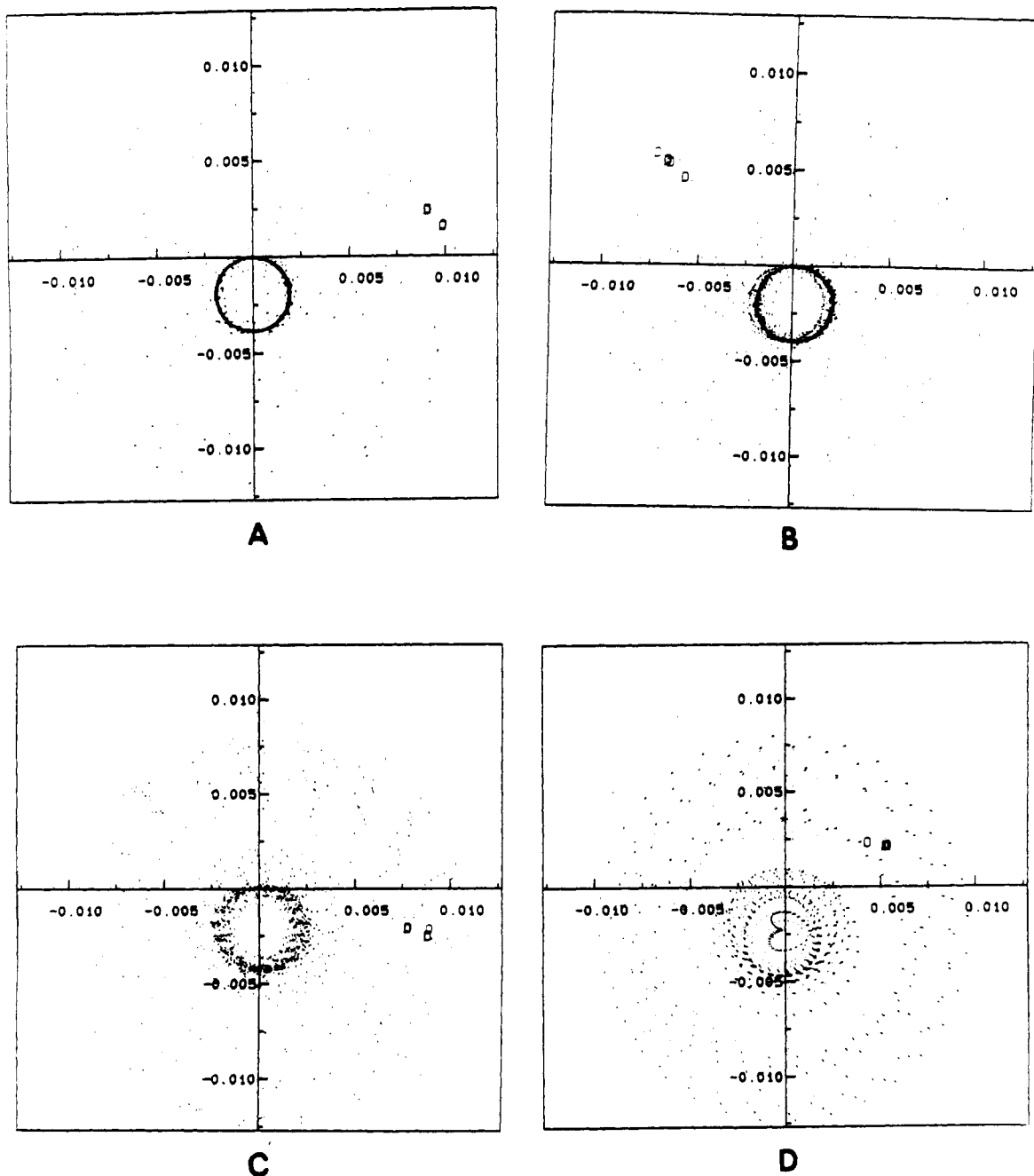


Figure 8. Four plots of temporal ion position (m/z 500, 3-T B field) as a result of ion excitation. The effect of frequency sweep excitation on the production of well-defined ion motion can be studied by computer simulations of ion motion. Frequency sweep synchronization of the ion population is evaluated by monitoring the dimensions of the ion packet following excitation solely as a function of the duration of the frequency sweep prior to resonant acceleration. (A) Ions accelerated by a frequency sweep initiated at a frequency corresponding to m/z 50. (B) Ions accelerated by a frequency sweep initiated at a frequency corresponding to m/z 100. (C) Ions accelerated by a frequency sweep initiated at a frequency corresponding to m/z 200. (D) Ions accelerated by a frequency sweep initiated at a frequency corresponding to m/z 300.

we attribute to phase synchronization) which presently limit the high mass analytical utility of FT-ICR.

One approach to addressing the problems arising from ions having significant initial radial velocities is through collisional relaxation of the ion's translational energy prior to excitation (34). Although this technique is effective for removal of excess translational energy, it introduces more complications into the FT-ICR experiment. For example, the high buffer gas pressures required to collisionally relax ions are incompatible with the ultrahigh vacuum required for detection by FT-ICR. Such techniques require removal of the collision gas prior to detection. Although pulsed-valve experiments of this type have been described, such experiments will not eliminate all the factors important in ion detection. For instance, collisional processes result in scattering of the injected ions. Ions having

initially high radial velocities which are scattered by collision with a buffer gas enlarge the spatial distribution of the ion packet, and the initial spatial distribution will be magnified upon rf excitation.

Off-resonant acceleration permits ions to interact with the electric field for extended periods without gaining translational energy. The ion ensemble is phase synchronized prior to excitation and therefore results in a detected packet of ions having more phase-coherent ICR orbital motion. The advantage of off-resonant excitation is that phase synchronization can be performed over a time period of many cyclotron orbits without a net gain in translational energy. The effect of off-resonance excitation has been observed experimentally and the net energy gained by the ion of interest can be neglected if the period of excitation corresponds to a node of

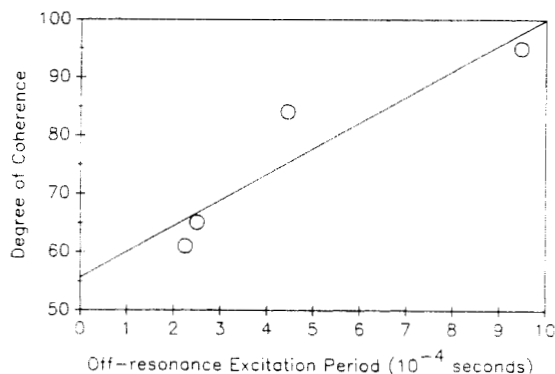


Figure 9. A plot of sweep duration vs the degree of coherence of the ion ensemble following excitation illustrates the effect of off-resonant acceleration.

the beat frequency produced by the difference between $\omega_{\text{cyclotron}}$ and ω_{applied} (35)

$$t = 1/|\omega_{\text{cyclotron}} - \omega_{\text{applied}}| \quad (2)$$

Thus, ions interact with a nonresonant rf electric field for a finite period and receive no increase in translational energy. The extended interaction of the electric field results in phase synchronization of the ion population prior to resonant acceleration. In theory, the extended interaction time of swept excitation and the associated increase in the spatial definition of the ion ensemble could be achieved by a single frequency, off-resonance acceleration prior to detection. The practical applications of this approach are now being evaluated.

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