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SPECIAL FEATURE: TUTORIAL

Windows Version of the Ion Trap Simulation Program ITSIM: a Powerful Heuristic and Predictive Tool in Ion Trap Mass Spectrometry

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The multi-particle simulation program ITSIM version 4.0 takes advantage of the enhanced performance of the Windows 95 and NT operating systems in areas such as memory management, user friendliness, flexibility of graphics and speed, to investigate the motion of ions in the quadrupole ion trap. New features and capabilities significantly broaden its applicability. The simulation program can provide help in understanding fundamental aspects of ion trap mass spectrometry and both precede experiments and assist in directing their course. It also has didactic value in elucidating and allowing visualization of ion behavior under a variety of experimental conditions. ITSIM 4.0 provides easy access to ion simulations for all users through a dramatically improved user interface. The program uses the improved Euler method to calculate ion trajectories as a numerical solution to the Mathieu differential equation. The Windows version can simultaneously simulate the trajectories of ions with a virtually unlimited number of different mass-to-charge ratios, up to a maximum of 600 000 ions, and hence allow realistic mass spectra, ion kinetic energy distributions, phase-of-ejection distributions and other experimentally measurable properties to be simulated. The simulated data are used to obtain mass spectra from mass-selective instability scans and by Fourier transformation of image currents induced by coherently moving ion clouds. Field inhomogeneities arising from exit holes, electrode misalignment, imperfect electrode surfaces or alternative trap geometries can be simulated with the program. Non-zero angle scattering in the hard-sphere collision model allows simulations involving collisional cooling to be performed. Complete instruments, from an ion source through the ion trap mass analyzer to a detector, can be simulated. Some typical applications of the simulation program are presented and discussed. Such features as the mass-selective instability scan mode, mass-range extension via resonant ion ejection, r.f. and d.c. ion isolation and non-destructive detection are shown. Comparisons are made between the simulated and experimental results, for example in mass-selective photodissociation. Fourier transform experiments and a novel six-electrode ion trap mass spectrometer illustrate cases in which simulations precede reduction to practice.

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INTRODUCTION

The quadrupole ion trap, a radiofrequency instrument introduced by Paul and Steinwedel[1] in 1953, has recently undergone dramatic changes. The invention of the mass-selective instability scan mode by Stafford *et al.*[2] was a key development leading to improvement in the performance of the ion trap as a mass spectrometer. Subsequent improvements in resolution,[3] mass range[4] and sensitivity[5] have made this an increasingly popular instrument. The significant contributions toward bringing ion trap technology into the field of biomolecular analysis[6,7] are the result of the compatibility of the ion trap with many different methods of ionization, including electrospray ionization,[8] laser desorption,[9,10] matrix-assisted laser desorption,[11–15] secondary ion mass spectrometry and fast atom bombardment.[16] The ability to store and manipulate ions in time rather than in space offers unique advantages over more traditional mass spectrometers, and MS^n capabilities are already a standard feature of commercial instruments. Ion traps have seen use in a variety of applications, from biochemistry[13,17] to environmental and process monitoring,[18] from fundamental studies of ion–molecule reactions[19] and ion–ion interactions[20] to ion structure determination.[21–23] Numerous reviews[5,24–28] describe the current status of the ion trap mass spectrometer and confirm its position as a versatile mass spectrometer of increasingly high performance.

The quadrupole ion trap is the three-dimensional analog of the two-dimensional quadrupole mass filter. The ion trap consists of three hyperbolic electrodes, the shapes of which are designed to produce a quadrupole field (Plate 1); the strength of which increases or decreases linearly in both the *r*- and *z*-directions. The

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oscillating quadrupole electric field is used to trap ions created within the device by injection of electrons or ions injected from an external source (Plate 2). The motion of the trapped ions in the quadrupole fields is described mathematically as solutions to the Mathieu equation. Ion motion can be expressed in terms that contain a set of frequencies described by the parameters β_z and β_r. If both the β_z and β_r values for an ion are <1, the ion will have stable motion. When the operating conditions are changed so that β_z or β_r reaches a value of unity for a particular ion, its motion becomes unstable and its excursion grows until the ion is ejected from the trap. The operating conditions in the trap can be described conveniently by the variables a and q which have a fixed but non-linear relationship to β and a linear relationship to the operating voltages and the m/z ratios of the ions. Thus,

$$q_z = -2q_r = \frac{8eV}{m(r_0{}^2 + 2z_0{}^2)\Omega^2} \tag{1}$$

$$a_z = -2a_r = \frac{-16eU}{m(r_0{}^2 + 2z_0{}^2)\Omega^2} \tag{2}$$

where V represents the maximum r.f. potential (zero to peak) and U represents the maximum d.c. potential applied between the ring and end-cap electrodes, Ω is the angular frequency of the r.f. drive potential, r_0 is the internal radius of the ring electrode, $2z_0$ is the closest distance between the two end-cap electrodes, m is the mass of the ion and e is the number of electronic charges it carries.

The device is physically small and simple, but the theory of ion motion is complex, so that with the growing importance of the quadrupole ion trap mass spectrometer, interest has increased in simulating ion motion within the device. Understanding of ion motion facilitates its control and should lead to enhanced performance of the ion trap which would further increase the power of this attractively simple instrument. Two contrasting procedures for characterizing ion motion have been explored. One employs experimental determinations of the time-dependent positions of the trapped ions, e.g. by laser tomography,[29] and the second method employs simulations of ion motion.

An early simulation study of a single ion in an ion trap was reported by Dawson and Whetten[30] in 1968. Numerical trajectories for ions formed with a variety of different initial conditions were used to predict resolution, sensitivity, storage time and peak shape. Ion trajectories and factors controlling their stability were addressed by March and co-workers.[31–32] The motion of a single ion during the mass-selective instability scan and the effects of resonant excitation on ion trajectories were explored in their studies. Franzen[33,34] introduced the effects of higher order fields in simulations of ion trapping and ion injection. He found that superimposed odd-multipole (hexapole) fields may be used for fast ion injection, whereas even multipoles (octapole) sharpen the ejection process. Vedel and co-workers[35–37] included space-charge and collision effects in their simulations. Simulations of the motion of single ions under additional d.c. fields, a.c. resonance excitation and the effects of buffer gas were investigated by March and co-workers.[38–40] Simulations of injection of single ions under different initial conditions at particular r.f. phase angles were reported by Chung-Sing and Schuessler.[41–45] All these simulations based insights into device performance on the examination of ion trajectories for single ions as a function of the initial conditions.

To refine ion simulations further, two multi-particle simulation programs have been developed in this laboratory to examine the behavior of collections of ions in the ion trap: ITSIM[46] runs on PC machines and NQS on parallel computers.[47] ITSIM has grown with advances in the PC platform and proven to be a valuable tool in simulations of the motion of ions in an ion trap. Simulations using this program were based on the quadrupole field associated with the ion trap electrode structure, initial ion positions were represented by Gaussian distributions and ionization events were randomly distributed over r.f. phase angle to yield a realistic collection of stored ions. The effects of collision with buffer gas and the ion–ion interaction were included in the program and activation via a resonant a.c. signal or a short d.c. pulse was introduced. The behavior of a small collection of ions could be examined, and followed by different display modes, including ion trajectory, kinetic energy, animation, phase space and Poincaré plots.[48] Memory limits of DOS-based 80 × 86 PC machines set the limits to the number of ions and recorded data points that could be simulated. The program was divided into small executable files, ITSIM, IONGEN and IONDAT, to adapt to the memory limits of DOS architecture. All files containing the generation, simulation, and scan-control parameters were ASCII files which could be edited by a user to create or to modify simulation experiments. This procedure required a large investment of time to learn the program and it was time consuming to take and export data. The program reached the limitations of DOS architecture and had no room for further development.

Given the value of the simulations and in response to changes in quadrupole ion trap technology, a Windows-based (Plate 3) multi-particle simulation program was developed to solve the problems of the previous DOS version. The latest version of the multi-particle simulation program, ITSIM 4.0, takes advantage of the performance of the 32-bit Windows operating system in areas such as memory management, user friendliness, flexibility of graphics and speed. It is written in C for Windows 95 or Windows NT operating systems and has 300 000 lines of code. The program is compiled by the Microsoft Visual C++ compiler, and integrated with the Quinn Curtis graphics library. Its new features and capabilities significantly broaden its applicability.

The program uses the improved Euler method to calculate ion trajectories as numerical solutions to the Mathieu differential equation. An extensive description and validation of the program will be published elsewhere.[19] The Windows version described here can simultaneously map the trajectories of more than 600 000 ions with a virtually unlimited number of different mass-to-charge ratios, and hence allows more realistic mass spectra, ion kinetic energy distributions and other experimentally measurable properties to be simulated. Non-zero angle scattering in the hard-sphere collision model allows simulations involving collisional cooling to be performed. The large number of simulated ions permits the examination of the combined effects of space-charge repulsion and collisional cooling. Complete instruments, from an ion source through the ion trap mass analyzer to a detector, can now be simulated. The simulated results are used to obtain a mass spectrum from mass-selective instability scans and to record distributions of other ion properties. Higher order fields associated with the driving r.f. field or auxiliary a.c. and d.c. potentials are also implemented in the new version. The simulated ion trajectories can be used to obtain frequency spectra by Fourier transformation of image currents induced by coherently moving ion clouds.

The user environment is highly interactive, allowing one to switch views, adjust voltages, calculate Mathieu parameters and check ion distributions while a simulation is in progress. Unlike previous DOS versions of ITSIM, this version is complete, i.e. IONGEN (a program used to generated ions), the main calculation routine ITSIM and IONDAT (a program used to process the simulated data) are all bound together in a single .EXE file. There is no need to keep track of or edit ASCII files. All the required parameters are managed through dialog boxes (Plate 4), providing easy access to the simulation program.

The primary goals embodied in the Windows version of the ion trap simulation program ITSIM 4.0 are to allow modeling of the behavior of a large number of ions in the quadrupole ion trap mass spectrometer and to allow the visualization of ensembles of ions to give insight into the character of their trajectories. The Windows version extends these capabilities further to the motion of ions in quadrupole traps of different geometries.

IMPLEMENTATION

The Windows version of the ITSIM simulation program has only a single executable file. Before a simulation can start, initial conditions of an ion population must be generated. There are three ways to generate the initial conditions: impulse, uniform or Gaussian distributions. The impulse function allows users to give ions particular positions, velocities and appearance times. Otherwise, initial ion spatial and velocity coordinates are distributed by the uniform or Gaussian distributions. A common spatial distribution for ions is a Gaussian distribution, centered about zero with a standard deviation determined by independent laser-tomography experiments.[29,50,51] The parameters for the Gaussian distribution can be checked prior to generation. The time when an ion appears (appearance time), is generated randomly within a user-specified time window. Ion velocities are distributed using the same method. It is important to distribute the velocity in a random fashion to prevent the trajectories from being artificially phase-locked. Once each ion has been assigned initial conditions, the program saves the ion data set to a binary file which is used by each subsequent simulation (Plate 4).

All the data needed for a simulation are loaded when a user commences an experiment. The ion trap internal radius, the higher order fields parameters and the r.f., a.c. and d.c. characteristics are edited in the instrumental dialog box. The simulation time, integration time, acquisition time and sampling rate are adjustable. Collision parameters include buffer gas diameter, pressure and temperature, and they can be adjusted in a collisional dialog box. Space-charge calculations can be turned on or off using a check box. Both frequency and amplitude variation are possible for the r.f. and a.c. scans. There are four d.c. time event tables to edit, one for a quadrupole d.c. applied to the ring electrode and three for dipole d.c. fields applied in the three dimensions.

The ion data list is modified every integration time step during the trajectory computation, according to the above parameters. When all ions have left the trap or the pre-set simulation time has expired, the ion positions, velocities, collision counts and all current parameters which contribute to the electric field are then stored in the ion list. The data in the list can be extracted to obtain a conventional mass spectrum, ion kinetic energy distribution, ion spatial distribution, the distribution of r.f. and a.c. phases at ejection, distributions of r.f., a.c. and d.c. amplitudes at ejection and collision count distributions. One can extract the data for ions of a specified mass or for all masses. The generated ion list can also be examined in the same way prior to further simulations. The sum of ion positions can be recorded using a given sampling rate. The simulated image current can be Fourier transformed to produce a frequency spectrum of the ion population in three dimensions. All graphs can be changed to different formats and exported to other Windows programs. Capabilities are available for printing a graph with a title, subjects, keywords, comment lines and author name. The positions and intensities of the six highest intensity peaks are also listed for each graph. Zooming capabilities are provided.

Ion trajectories in one or two dimensions, ion velocities, kinetic energies, animations, phase-space plots and Poincaré sections can be viewed directly. There are eight different display modes to meet the complexities of the simulated results, as shown in Plate 3. The program allows a user to color-code ions of six different mass-to-charge ratios. A large number of ions can be simulated, but only 32 ions from any ion population are randomly selected for display in one-dimensional trajectory display modes and 16 ions are randomly selected for display in animation and two-dimensional trajectory display modes.

The Windows ITSIM program is easy to use: there is one main file for each experiment and new experiments are created in one step. All parameters are edited through dialog boxes. Experiments can be organized by the title, subject, keywords, author name, comments and data. Each dialog box directly connects to an appropriate on-line help file. The simulated data and graphical output can be printed, changed in format or exported to other Windows program.

APPLICATIONS

The motion of ions through a complete instrument, from ion source through the ion trap mass analyzer to detector, can now be simulated by using ITSIM. The ion trap simulation program has been used with considerable success.[46–48,50,52–59] Because of its new features and capabilities, some basic applications of the Windows version of the program are presented to illustrate its broad applicability. A detailed description of performance and advanced applications of the program are presented elsewhere.[60]

Ion motion

Despite the simplicity of the quadrupole ion trap, the trapped ion motion is complex. In a pure quadrupole field, the ions are trapped in the radial (r) direction by a cylindrical oscillator and in the axial (z) direction by a planar oscillator. Therefore, ions move independently in the z and r directions. Motion is described by the Mathieu equation, the solution to which can be expressed as an infinite series of sine and cosine terms. Ions in the trap move under the influence of the r.f. trapping field and supplementary d.c. and a.c. fields. The ion trap constrains a large number of ions in a very complex environment which includes collisions with neutral gas, ion–ion interactions and imperfect electric fields. The resulting conditions are not adequately represented by the analytical solutions to the Mathieu equation. Even in the ideal case, ion motion in the trap is described by a set of frequencies which includes a number of higher order terms. Trajectories of two ions of m/z 269 and 69 in the x–z and x–y planes are shown in Plate 5. In the simulation, the two ions are trapped by a fixed r.f. amplitude corresponding to q_z values of 0.180 and 0.702, respectively. The ions display characteristic behavior, including a distinctive set of frequencies, under given operating conditions. The trajectory of the low-q_z value ion in the x–z plane describes a Lissajous figure (Plate 5). However, the motion of the higher q_z value ion is more difficult to describe, although it is still controlled by a characteristic set of frequencies.

Mass-selective instability scan

The mass-selective instability scan, first described by Stafford *et al.*,[2] transformed the ion tap into a valuable mass spectrometer. The scan involves ramping the r.f. amplitude so that ions of increasing mass-to-charge ratio are sequentially ejected and detected by an electron multiplier. Plate 6 shows ion trajectories, the corresponding ion kinetic energies and the voltages applied at the electrodes during a mass-selective instability scan. In this experiment, the trap contains 400 ions with m/z of 43, 700 ions with m/z of 51, 1700 ions with m/z of 77, 2000 ions with m/z of 105 and 700 ions with m/z of 120, a collection which is roughly representative of the ions formed from the dissociation of the acetophenone molecular ion. A Gaussian distribution of initial positions and zero initial kinetic energy is used to represent the cooling of this population prior to the mass analysis experiment. The small right-side window displays all the current parameters used for the simulation. The top box in the main windows displays time-dependent values of r.f., a.c., quadrupole d.c. and x-, y-, z-dipole d.c. voltages, with the display ranges independently scale for the r.f., a.c. and d.c. voltages. The next two boxes show the ion trajectories in the radial and axial directions, respectively. The last box in the main window displays the temporal dependence of ion kinetic energy. The lightest trapped ions, m/z 43, have the highest, q_z value at given r.f. amplitude. As the r.f. amplitude is increased (the top graph in the main window), the q_z value of each ion increases, moving closer to the z-stability boundary value of 0.908. As ions reach this instability border, their excursions in the axial direction become larger than the dimensions established by the end-cap electrodes and some are ejected through holes in each end-cap. At the ejection point, time, r.f. amplitude and all current parameters are recorded for each ion. The r.f. amplitudes at the ejection points of all ions are used to calculate their mass-to-charge ratios [e.g. from Eqn (2)] and are extracted to form a mass spectrum as shown in Plate 7. The top graph is the stimulated mass spectrum and the bottom graph zooms in on the m/z 77 peak. The peak intensities and positions of the most abundant ions (up to six) are also displayed.

R.f./d.c. isolation

Isolation of ions of a particular mass-to-charge ratio is the first step in a tandem mass spectrometric (MS/MS) experiment. An r.f./d.c. isolation experiment is illustrated in Plate 8. In this experiment, ions of three different mass-to-charge ratios, m/z 83, 91, 165, are initially distributed in a Gaussian fashion in the trap. By applying (upper box) an appropriate combination of r.f. and d.c. potentials to the ring electrode, the ions to be isolated, m/z 91, move to the upper apex of the Mathieu stability diagram. First, the r.f. amplitude is increased so that the q_z value of the ions of the mass-to-charge ratio of interest reaches 0.78, the q_z value of the upper apex. Second, a negative d.c. pulse is applied to bring the a_z value of these ions to 0.15, the a_z value of this apex point. Ions of interest are still in the stable region near the apex, but all other ions have been forced into the adjacent unstable regions. All ions of lighter mass (blue ions) than the ions of interest are z-unstable, and those ions of higher mass (green ions) are r-unstable. Only the selected ions (magenta ions) are stable in both the axial and radial dimensions and remained trapped

A.c. excitation

Using the standard capabilities of the original commercial ion trap mass spectrometers, the mass-to-charge range of the instrument is about m/z 650.[61] Clearly, this is inadequate for many experiments using biomolecules. The mass-to-charge range can be extended through resonant ejection in which an instability point is created at a q_z value much lower than the normal ejection value of $q_z = 0.908$.[62] In these experiments, a supplemental a.c. signal is applied to cause ions of a selected q_z value and associated secular frequency to be resonantly excited and ejected. Resonant excitation by an a.c. signal can also be used in a similar manner to improve the resolution[63] or to cause translational excitation and hence collision-induced dissociation of the selected ions in the presence of buffer gas.[61] Plate 9 is a display of an a.c. excitation experiment involving a group of ions of *m/z* 1000, 2000 and 3000. Before the supplementary dipole field is applied, the amplitude of the main r.f. is such that all three groups of ions undergo stable motion in both the *r* and *z* directions. When an a.c. frequency is applied that matches the secular frequency of the ions of interest (*m/z* 2000 in this case), these ions resonate with the applied a.c., acquire energy and are ejected whereas the lighter and heavier ions remain stable. The increase in the axial displacement and kinetic energy of the ions of interest is shown in the two bottom windows in Plate 9. The fact that the motion of all three groups of ions remains stable in the radial direction throughout the application of the dipolar a.c. signal is illustrated in the second box.

Information on the stability and periodic nature of the behavior of the entire collection of ions under the effect of a.c. excitation is efficiently represented in a Poincaré section[64] or by phase-space plots. Phase-space plots have proven to be a valuable tool in analyzing the dynamics of the ion trap for some time.[65] In these plots, the ion velocity is plotted as a function of position. Phase-space plots are constructed in real-time, whereas the more recently applied Poincaré sections[7] are sampled at the r.f. drive frequency and at a chosen phase angle. Because of this, the phase-space plot is used to examine both the secular motion and the micromotion of an ion, whereas the Poincaré section can be used to describe the secular motion of an ion independently of micro-motion due to the driving r.f. field. For example, in a pure quadrupole field and in absence of collision, the Poincaré sections of motion of ions consist of a set of ellipses. Plate 10(A) gives an example of an axial phase-space plot and Poincaré section for one ion placed at the center of the trap with zero kinetic energy and subjected to a.c. excitation. The increase in axial (*z*) position and velocity is shown by the enlargement of the ellipse in the Poincaré section and of the contour in the phase-space plot. As the ion absorbs energy from the auxiliary field, the limit cycle increases in diameter until the electrode dimension is reached and the ion is lost.

When the a.c. signal applied at the endcap electrode is low and prolonged, ions maintain their phase coherence, which results in high mass resolution. Typically, the a.c. frequency is chosen to give a convenient mass-range extension factor and beating between the main r.f. drive and the resonance a.c. signal occurs, [Plate 10(A)]. A fixed phase relationship between the two signals is desirable to improve performance[47] and Plate 10(B) shows the same experiment, but with the r.f. drive and a.c. signal phases now locked, the a.c. frequency having an integral relationship (1 : 4) to the r.f. frequency. The Poincaré section and phase-space plot now show a linear increase of excursion and velocity with time which is associated with fixed-phase resonance ejection. Under the fixed-phase ejection conditions, the initial r.f./a.c. phase angle can be chosen such that the critical r.f./a.c. phase relationship occurs every a.c. cycle. The linear increase in excursion and velocity of the ions of interest during r.f./a.c. excitation promises greatly enhanced resolution.

D.c. excitation and non-destructive detection

Unlike a.c. excitation methods which excite only ions of a particular mass-to-charge ratio of interest, a short d.c. pulse can be used for broadband excitation. Plate 11 shows the ion motion induced by impulsive excitation. Three 10 V, 2.7 μs dipolar d.c. pulses are applied to a group of ions with different mass-to-charge ratios, with a Gaussian distribution of initial positions and randomly introduced into the trap within one r.f. cycle. The ions are excited almost instantaneously into coherence in all three directions. The d.c. potential applied to the end-cap electrodes excites ions in the *z*-direction, whereas the two d.c. pulses applied to a segmented ring-electrode force ions into coherence in the *x*- and *y*-directions. The novel segmented-ring electrode is discussed further later and presented in more detail elsewhere.[55] Ions with different mass-to-charge ratios are separated in all three directions. The simulation shows that the motion of the excited ions is remarkably stable, even in the presence of helium at a pressure of 1 mTorr (1 Torr = 133.3 Pa). These and related observations suggest a non-destructive detection mode[54] in which impulsive excitation is followed by detection of the image current. The program is able to simulate the image current induced by the ion clouds by recording all the *z*-positions of the ions at each sampling interval. Plate 12 is a result from a simulation of the image current of a single ion of *m/z* 91 and one of *m/z* 92 at q_z values of 0.266 and 0.263, respectively. The beat signal is the point in time at which the ions are separated in phase by 180°. The decay of image current density with time is caused by collisions with the helium buffer gas. The time-domain signal is transformed into the frequency domain spectrum also shown in Plate 12. The list of the peak positions in the frequency spectrum and their intensities is displayed in the right corner of the window. The bottom graph displays a close-up view of the two peaks in the frequency domain. This experiment demonstrates the strong, mutually complementary inter-relationship between simulations with ITSIM and ion trap experiments. The broadband non-destructive detection experiment with first simulated[54] and then demonstrated in practice.[56]

A novel six-electrode quadrupole ion trap mass spectrometer

The simulation program has been used to characterize a novel trap geometry, an ion trap mass spectrometer with a segmented ring electrode. A brief description of the simulations is presented here as an application of ITSIM; a detailed study is presented elsewhere.[55] Simulations suggesting the value of the novel geometry are shown in Plate 13. When an ion is generated with zero initial velocity, its three-dimensional motion is confined to a plane, corresponding to a line in the *x*–*y* plane, as shown in Plate 13(A). On the other hand, if the ion has initial velocity in the axial direction when generated, it will experience larger oscillations in the radial direction [Plate 13(B)]. The projection of the ion trajectories in the *x*–*y* plane displays an elliptical orbit,[57] because the kinetic energy in the radial direction launches the ions into an orbit around the center. Ions introduced into the trap through apertures in the end-cap electrode, or generated by electron impact, do not have significant radial velocity. Thus, each ion moves approximately in a plane which is defined by its initial position and its r.f. phase at injection. The segmentation of the ring electrode into four sectors is designed to achieve three-dimensional control of the motion of these trapped ions. The six-electrode ion trap mass spectrometer allows application of d.c. voltages so as to excite an ensemble of ions in the radial direction.

These simulations suggest that an ion population excited in both the radial and axial directions occupies more of the available volume in the trap. This can be seen in Plate 14. The contour plots (ion intensity *vs.* position) in the x–z plane show the more dispersed ion population produced by a radial d.c. pulse. Even though the density of ions of a given m/z value appears to increase, the space charge effects between ions with different mass-to-charge ratios should be reduced. Application of the three dipolar d.c. pulses in three dimensions forces ions with the same mass-to-charge ratio to move coherently in three dimensions. The separation in space of ions with different mass-to-charge ratios, achieved by the three d.c. pulse excitations, is shown in the animation plot in Plate 15. An increase in mass resolution of the ion trap mass spectrometer might be expected to occur in both the destructive and non-destructive modes of detection.

The fact that coherent motion of ions in two orthogonal directions can be achieved by applying two d.c. pulses, one between the end-cap electrodes and the other across the segmented ring, suggests the possibility of a two-dimensional Fourier transform experiment (Plate 16). Owing to the higher order field components which are distributed unevenly inside the trap,[66] the relationship between the frequencies in the two directions can be expected to be somewhat different. Simulations of two-dimensional FFT signals of the two ion species, m/z 91 and 92, with higher order field components are shown in Plate 16. The case shown is that for a 2% octapolar field where the two peaks overlap in the axial direction while they remain well separated in the radial direction. It is likely, therefore, that information on the distribution of higher order fields inside the ion trap might be available from such two-dimensional Fourier transform ion trap mass spectra.

Mass-selective photodissociation

Taking advantage of the fact that the Windows version of ITSIM can simultaneously follow the motion of a large number of ions, a simulation of the ion distribution inside of the trap during photodissociation can be performed. This simulation employs an axial quadrupolar d.c. pulse to force 20 000 ions into coherent radial motion. Ions of the same mass-to-charge ratio are all either in phase or phase shifted by exactly 180°. All the ions continue to oscillate at their secular frequency in a coherent fashion after the impulse is removed, so that ions of the same mass-to-charge ratio cross the z-axis at the same time. At other times, these ions are dispersed to varying extents in all three dimensions. Ions with different mass-to-charge ratios cross the z-axis at different times, owing to the differences in their secular frequencies. At the specific moment at which ions with the same mass-to-charge ratio cross the z-axis and the ions with other mass-to-charge ratios are dispersed in the radial direction, and a single pulse laser beam, aligned collinearly with the z-axis can be used to photodissociate mass selectively the ions crossing the axis (Plate 17). An experiment was performed to test this prediction by seeking an increase in photodissociation efficiency by appropriately timing the laser shot.[50] This experiment successfully demonstrated the ability to perform mass-selective photodissociation in an ion trap mass spectrometer without actual isolation of the ions of interest.

For a more detailed comparison of simulation and experiment, 10 000 ions of m/z 105 and 10 000 ions of m/z 150 were used to simulate ion distributions inside the trap. The number of ions at the center of the trap as a function of time is displayed in Plate 18. It can be seen that this number varies periodically for m/z 105 and 150, and it is explicitly confirmed that the frequencies are mass dependent. Therefore, at a particular time, the number of ions with the same mass of interest at the center of the trap is a maximum and that of the other ions is near its minimum. The number of ions within a cylinder of 0.6 mm diameter (diameter of the laser beam) in the radial direction of the center of the trap corresponds to the number of ions in the path of the laser and is therefore expected to be proportional to the photodissociation efficiency in the laser photodissociation experiment. The simulated plot of the number of ions at the center of the trap *vs.* time agrees well with the experimental photodissociation efficiencies as a function of delay time between the d.c. pulse and the laser pulse.[50]

CONCLUSION

The program ITSIM 4.0, a 32-bit Windows-based program, uses an improved Euler method to calculate the trajectories of a large number of ions as a numerical solution to the Mathieu differential equation. These simulations are the first which can follow the motion of a large ensemble of ions in an ion trap. With eight different display modes and different colors for each mass-to-charge ratio, the program significantly enhances visualization in describing the complexities of ion motion. The simulations are extended to include the effects of actual operating conditions and this leads to the development of new operating modes and associated refinements in instrumentation. The simulation program allows new experiments to be explored without a large investment of time and money: simulations suggest new experiments, illuminate the results of experiments and serve as an educational tool.

The non-destructive broadband method of detection was first examined using ITSIM[54] before experiments with the actual ITMS proved the feasibility of this new operational mode.[56] When used in conjunction with a field-calculation program such as POISSON, ITSIM can take field inhomogeneities into account. Thus, the behavior of ions in traps with different geometries can be simulated. Simulation of ion motion in a cylindrical trap is currently being explored.

Various steps can be taken to extend the performance of the simulation program, and some of these are under way, including direct integration with the POISSON program to simulate behavior in traps with different geometry. An improved simulation time calculation routine for space-charge effects is currently being investigated. Future work will address quasi-real-time three-dimensional representation[57] of ion motion. The program will also be extended to accept SWIFT[67,68] or other waveforms that a user might apply to the end-cap electrodes. Further emphasis will be placed on improving the collision models to cover the use of mixtures of neutral bath gases, and to include inelastic collision effects. Later, the program will be extended to have an MS/MS predictive capability in conjunction with RRKM calculations.

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