Detailed simulation of mass spectra for quadrupole mass spectrometer systems

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A method of computation to determine the trajectories of large numbers of ions in quadrupole mass spectrometers has been developed. The computer program produces simulated mass scans with over 10^5 ions injected into the quadrupole model at each point on the mass scale. The computation method has been combined with an improved representation of an ion source to predict the behavior of complete quadrupole systems; the results obtained are shown to reproduce most features of experimentally observed mass scans. The calculations show that the shape and height of mass peaks depend strongly on the properties of the ion source. However, ion source properties have a relatively small effect on the resolution of the mass spectrometer and an alternative to the common method of presenting the resolution of a quadrupole is proposed. This alternative better indicates the performance of the instrument as it is less sensitive to effects of the ion source. Results are also presented which indicate that peak splitting, closely matching experimental observations, can be produced by small changes in the exit aperture of the quadrupole. © *2000 American Vacuum Society.* [S0734-2101(00)00801-0]

I. INTRODUCTION

Applications of quadrupole mass spectrometers range from analysis of simple gas mixtures with low resolution systems to analysis of complex organic materials using high resolution devices. A comprehensive review has been given by Dawson.[1] There have been a number of analytical attempts to predict performance and determine the effect of adjusting various parameters. The first analysis which predicted many features of quadrupole behavior was a matrix method;[2] computational facilities available when this was performed restricted the range of situations examined.

The advent of high speed, large memory personal computers allows finite length quadrupole mass spectrometers to be simulated without high computation service costs. Batey,[3] Ma and Taylor,[4] and Voo *et al.*[5] showed that some features of the behavior of the quadrupole, when operated as a mass filter, could be predicted by tracing the motion of ions through the filter. These authors suggested that it was sufficient to trace the trajectories of a few hundred ions through the quadrupole filter. While this allows some features of quadrupole behavior to be identified we have found that more detailed prediction of the behavior requires that the trajectories of a much larger number of ions must be examined. This is particularly important for instruments operating at high resolution and low sensitivity (only a small proportion of ions pass through the filter) and for modern very short length quadrupoles.[6] The original program of Voo *et al.* could not be adapted to handle significantly larger numbers of ions. The computation time to determine each trajectory was too long and the large data structures necessary for many ions could not be created by the compiler.

This article reports results using an entirely new program written in the C^{++} language.[7] In addition to overcoming the limitations of the earlier program it includes many additional features. During development of the new program, it was found that use of regular intervals in either the time or position of ion entry to the quadrupole sometimes produced anomalous results. Consequently, the model used to simulate the entry of ions into the filter has been refined to significantly improve the representation of the combined behavior of ion source and quadrupole system. The program produces results for a simulated mass scan with between 10^5 and 10^6 ions traced at every point on the mass scale. A large number of mass scale points may be selected and the program will operate in an acceptable time for most situations of interest. Computation time varies significantly with the dimensions of the quadrupole and with the operating conditions; for a typical medium resolution system results using 200 000 ions at each of several hundred mass points can be obtained in about 10 h using a personal computer with an Intel Pentium type 400 megahertz CPU.

Simulation results are presented and compared with experimental results. They apply for operation when the ion mean free path is long compared with the quadrupole dimensions, generally for pressures below 10^{-4} Torr. It is assumed that the ion density is low enough to ignore space charge effects (usually true for operation of a quadrupole filter).

II. MODEL

A. Ion generation

The revised computer model simulates the generation of ions in a manner that is a better representation of ion generation by a hot filament source typically used in residual gas analysis.[3] Ions are assumed to originate at any point on a circular disk centered on the quadrupole axis and set at right

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angles to the axis. The quadrupole field starts immediately when the ions leave the source. The fields between the source and quadrupole are ignored. Ions are detected if they pass through a circular disk at the exit of the filter, again fringe field effects are ignored. The radii of both source and exit disks may be different and varied freely.

The program generates each ion at a point in the source disk selected at random with no correlation between the points used for successive ions; all positions are equally probable, this corresponds to uniform source illumination. The time of origin in the source is also selected randomly; that is ions enter the quadrupole at random values of the phase of the radio frequency voltage, the alternating current (ac) voltage, used to operate the filter. It is common practice to describe the quadrupole filter with respect to a set of rectangular Cartesian axes[5] with the z axis as the axis of symmetry parallel to the rods; the x and y axes each intersect the centers of a pair of opposing rods. When generated, ions are assumed to have the nominal energy set by the applied accelerating voltage in the source and their velocity is assumed to be entirely in the z direction; i.e., the velocity components v_x, v_y, and v_z are

$$v_x = v_y = 0; \quad v_z = \left(\frac{2eA}{m}\right)^{1/2}, \tag{1}$$

where e is the ion charge, m its mass, and A the accelerating voltage.

B. Computation of ion propagation

Ions travel through the filter with constant velocity in the z direction. This is because the fringe fields have been ignored and all the electric fields experienced by ions are at right angles to the z direction; therefore there is no component of force to change the velocity in the z direction. At any time when the magnitude of either the x or y coordinate of an ion exceeds the filter radius, r_0, it is rejected. Ions that pass through an exit aperture form the received signal.

Ions are traced through the filter by determining their motion in the hyperbolic field. Their travel is divided into small time intervals and their motion over each small time interval is computed using the local field they experience (the field is function of time because the applied voltage includes an ac component). The motion is approximated using a fourth order Runge–Kutta algorithm. The program was tested by increasing the time step from a small value to one corresponding to about 0.05 of the period of the applied voltage without any significant change in the results being observed. Even larger step sizes caused only minor variations in the results.

The fourth order Runge–Kutta algorithm is often selected to solve equations of motion as it is easily applied to second order differential equations. The insensitivity to step size suggests an even less complicated algorithm may be sufficiently accurate to determine ion motion in the mass filter. If this is correct, implementation would allow the program speed to be further increased.

C. Mass scale

A quadrupole filter is operated by simultaneously varying the amplitudes of the direct current and ac voltages, U and V respectively, which are applied to the rods. The actual values of U and V set the operating point on the instrument's mass scale while the resolution is set by choice of the ratio of U to V. The instrument is operated to produce a mass scan by varying both U and V while keeping the ratio of U to V constant.

When a quadrupole is constructed, the mass scale is usually determined by calibrating the instrument using a known mixture of gases in the source. For the computer model the scale is defined by assuming that the value of the amplitude of the ac voltage, V, corresponds to the peak of the stability diagram.[2] The peak occurs where $q = 0 \cdot 706$ and $a = 0 \cdot 23699$ using definitions $q = 2eV/m\omega^2 r_0^2$ and $a = eU/m\omega^2 r_0^2$; ω is the angular frequency of the ac voltage where $f = \omega/2\pi =$ the frequency of the ac voltage (all quantities are in System International units). Defining the mass scale by assuming that the value of V corresponds to the peak of the stability diagram gives

$$m = \left(\frac{2e}{0 \cdot 706\omega^2 r_0^2}\right) V. \tag{2}$$

Values of m are usually given in atomic mass units (amu) obtained by multiplying the value in Eq. (2) by $5 \cdot 9769 \times 10^{26}$. For computed results the resolution setting is expressed as the U to V ratio which is represented by η; the linear scale for η is defined such that at the stability diagram peak corresponds to $\eta = 1$. That is the peak is when $a = 0 \cdot 23699$; if the mass scale defined as above then $\eta = 1$ when

$$U = 0 \cdot 1678V = \frac{0 \cdot 05923\omega^2 r_0^2 m}{e}. \tag{3}$$

D. Quadrupole "size"

The earlier work[4,5] demonstrated that the resolution of a quadrupole primarily depends on the number of cycles of the ac field experienced by ions during the transit through the filter (that is the time in the filter multiplied by the frequency). This number of cycles is

- proportional to the frequency of the ac field
- proportional to length of the filter
- proportional to velocity of ions in the z direction; from Eq. (1) this is proportional to the square root of the accelerating voltage, A, and inversely proportional to the square root of the ion mass, m.

All our results confirm that the behavior depends strongly on the number of cycles. Changing several parameters simultaneously to obtain results for filters of different physical size but in which ions to experience the same number of ac field cycles produces almost identical results.

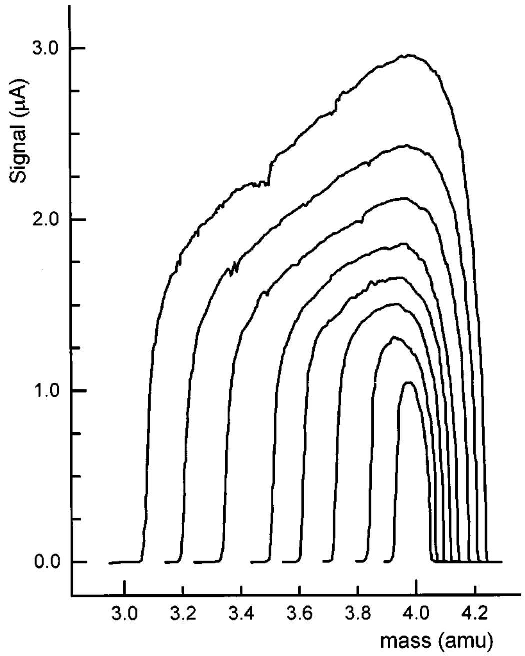

FIG. 1. Experimental recordings of the He^+ mass peak for equal steps in the setting of the resolution control.

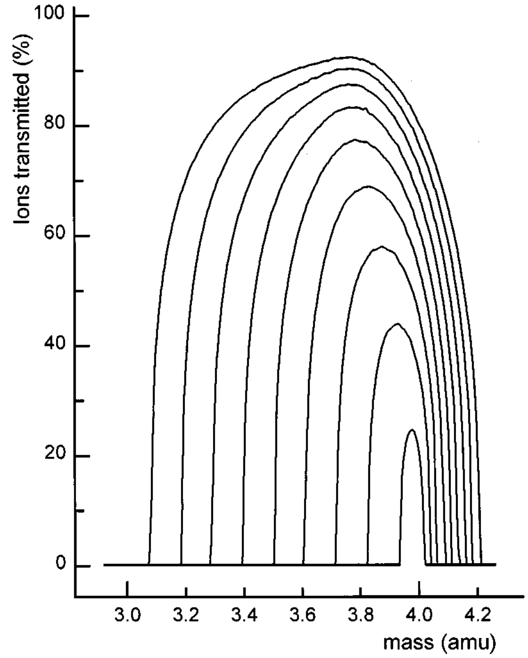

FIG. 2. He^+ mass peak computed with equal steps in η, the resolution.

III. RESULTS

A. Simulation of a single mass peak

Figure 1 shows mass peaks obtained experimentally with a high resolution quadrupole filter. It has length=228.6 mm, $r_0=5.54$ mm, $f=8$ MHz; the ions used are He^+ with mass 4 amu, and the ion energy is 2 eV. The ions experience about 189 cycles of the field when traveling through the filter. In the figure the peaks were produced by making equal step changes in the resolution control setting (corresponds to equal steps in η for the model).

Figure 2 shows computed results with equal steps in η. Amplitudes were computed at equal mass steps of 0·01 amu with 2×10^5 ions traced at each mass point. The amplitude scale indicates the percentage of ions that leave the source and reach the detector. Close examination shows small fluctuations, the curves are not perfectly smooth; the fluctuations are consistent with the statistical variations expected when the ions are generated at random positions in the source and at times such that entry to the quadrupole is random with respect to the phase of the ac voltage. There is good agreement between the computed and experimental results for resolution over the whole range.

Although they have similar features, the peak shapes of experiment and model are not identical. However, it was found that minor changes to the model can cause large changes to peak shape and height. Figure 3 shows a second set of results for the model, resolution remains almost the same but the peak heights (the amplitude scale is expanded when compared with Fig. 2) and shapes have changed. The only difference between results in the two calculations is that different radii were used for the uniformly illuminated ion source; the radius for Fig. 2 is $\frac{1}{4}r_0$ and for Fig. 3 it is $\frac{2}{3}r_0$.

The ion sources used for both Figs. 2 and 3 will not be an accurate representation of any real ion source. The variation of peak height and shape with relatively minor changes in the representation of the ion source suggests that a more elaborate model of the ion source must be devised if a theoretical model is to reliably reproduce experimentally observed peak heights and shapes.

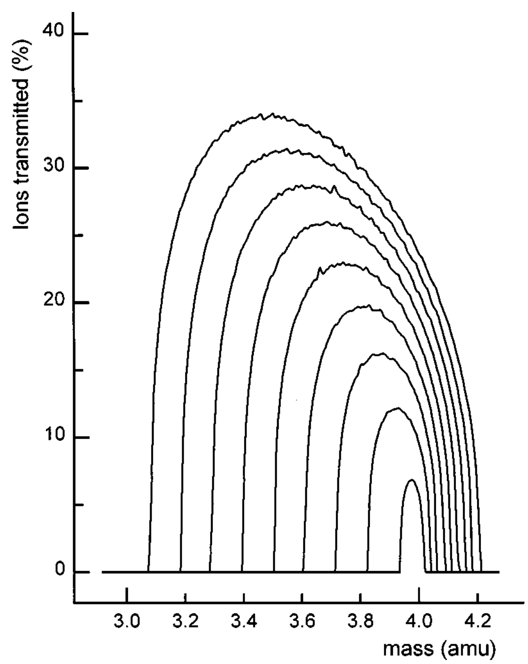

FIG. 3. He^+ mass peak computed as in Fig. 2 but with the ion source radius increased to $\frac{2}{3}r_0$ from $\frac{1}{4}r_0$ (same total ion current).

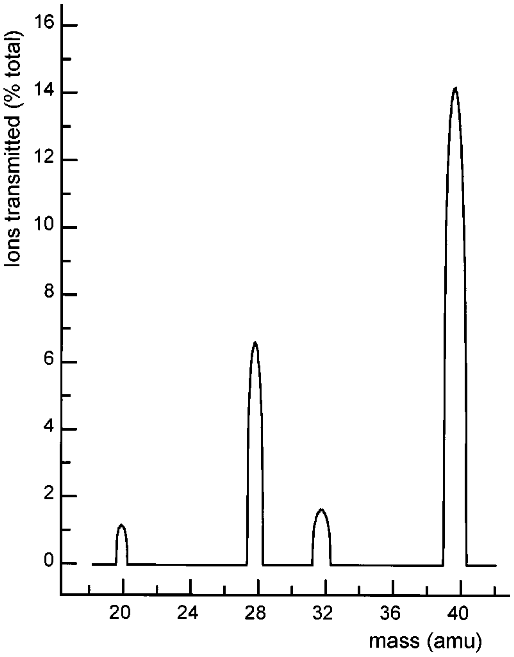

FIG. 4. Computed mass spectrum for an ion source producing four types of ion simultaneously.

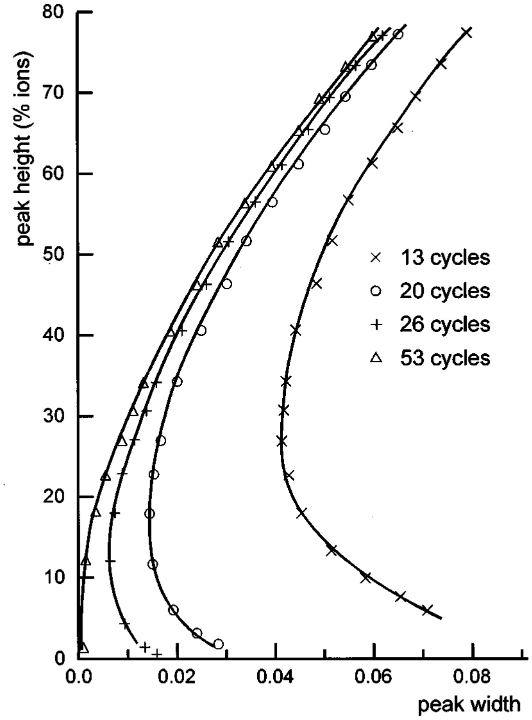

FIG. 5. Computed peak width, ΔM, as a function of peak height for quadrupole filters in which He^+ ions experience different numbers of cycles of the ac field.

B. Simulation of a spectrum containing several mass peaks

Figure 4 shows the results produced by the model for a mass scan when the ion source produces a mixture of several ions. The results are for a medium resolution instrument with a length of 127 mm, $r_0 = 2.768$ mm, $f = 4$ MHz and an ion energy of 2 eV. A total of 500 000 ions were injected into the quadrupole at each of 1000 different points on the mass scale. The mixture of ions is given in Table I; the table also indicates the number of ac cycles each type of ion experienced and the number of ions of each type transmitted at the respective peak positions. The total run time to produce the figure was about 10 h.

C. Computations of quadrupole resolution

Figure 5 shows results for peak height, given as percentage of ions transmitted, against peak width for a number of quadrupole systems using He^+ ions. Peak width is an indication of quadrupole resolution. The definition of peak width is not critical; the one adopted is that the peak width, ΔM, is the width at 10% of the peak height. The number of ac cycles seen by transmitted ions is the primary cause of the difference between the results and is used to differentiate the sets. As indicated previously almost identical results are obtained for different situations (length, frequency, mass, and energy combinations) which give the same number of cycles.

TABLE I. Data for the computed mass spectrum of Fig. 4.

Ion type and effective mass (amu)	ac cycles seen by ion	Total number of ions at each mass point	Percentage of ions transmitted
Ar^{++} 20	116·1	25 000	24·5
N_2^+ 28	137·3	140 000	24·1
O_2^+ 32	146·8	35 000	24·6
Ar^+ 40	164·1	300 000	24·3

Figure 5 shows the results for peak width as a function of peak height; this is the form presented previously.[3,4] Figures 2 and 3 illustrated that changes in ion source properties may change both the peak shape and height; however, such changes do not significantly alter the peak width at 10% of the height. Consequently, graphs of the form of Fig. 5, showing peak height as a function of peak width, change when ion source conditions change. However, the ability of the quadrupole to resolve adjacent mass peaks does not vary significantly with such changes. A better approach is to show η as a function of peak width; results used for Fig. 5 are shown in this alternative form in Fig. 6 (the scale for η is in a reverse sense for comparison purposes). This use of η as a parameter gives a representation of quadrupole resolution that is not strongly affected by variations in ion source conditions. We suggest that the relationship between peak width and η should be used, rather than that between peak width and height, to describe the resolution of a quadrupole.

Generally, as quadrupole resolution improves, the peak width decreases while the peak height decreases. However, experimental results[1,4,6] show some cases where the width stops decreasing as peak height decreases; in some cases the width increases (resolution becomes worse) as the peak height is further reduced. Comparison of the two forms of presentation of results indicates the cause of this observation. The effect occurs for filters in which ions experience rela-

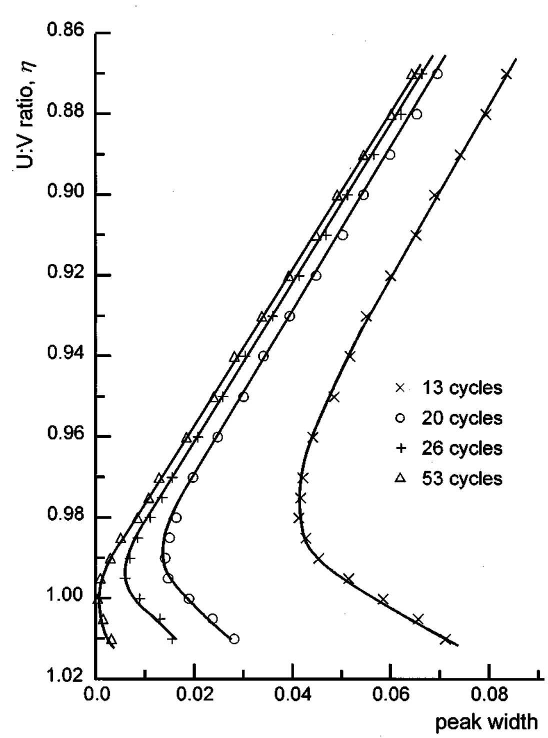

FIG. 6. Computed peak width, ΔM, values of Fig. 5 as a function of the quadrupole resolution setting, η.

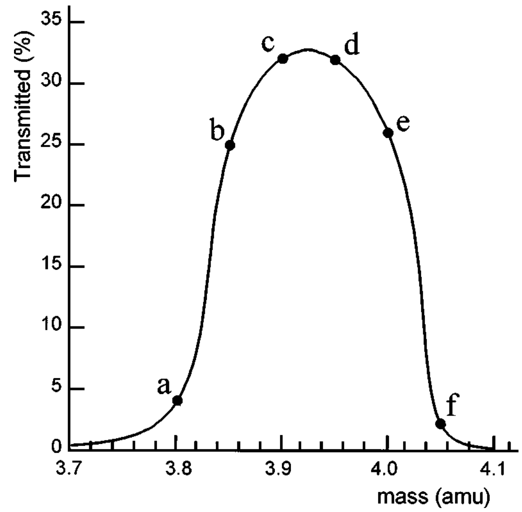

FIG. 7. He^{+} mass peak computed for a moderate resolution quadrupole, labeled points correspond to those used for the *contour* maps of Fig. 8.

tively few cycles of the ac field with η very close to $\eta=1\cdot0$; that is near the peak of the stability diagram. The two forms of presentation also indicate that for high resolution filters (ions experience many cycles in the filter) peak heights become extremely small as η increases towards $1\cdot0$). The highest value of η at which any ions could be transmitted decreased as the number of cycles increased.

Examination of the detailed results of the analysis for a wide range of quadrupole systems shows that the decreasing resolution (increasing peak width) at very high resolution is a function of the exact peak shape. For a system in which the ions experience many cycles of the ac field the peaks have a relatively flat top; as η is increased from a relatively low value the shapes of the low and high mass sides of the peak stay almost constant and the width of the relatively flat top of the peak decreases. That is, as the resolution improves the two sides of the peak move together but there is no change in the shapes of the sides. Close to $\eta=1.0$ the peak top is no longer flat and the height reduces rapidly as η increases because the two sloping sides continue to move together. The exact change in width depends strongly on the precise shapes of the two sides. If the system is such that ions only experience a small number of cycles the peak is never flat topped, even at very low values of η, and the shape changes in a complicated manner as η increases.

D. Investigation of source effects

One version of the new program includes a trace facility. This allows many details of every ion which reaches the detector to be recorded; the record holds starting position in the source, start time which is equivalent to the phase angle of the ac voltage when the ion enters the filter, and other details.

Using this information it is possible to determine the point of origin in the source for each ion that reaches the detector. This has been performed for many systems with a range of resolution, all produce results leading to similar conclusions. However, illustrations that demonstrate this behavior are most easily understood if the resolution used is not too high.

The system used for the example results presented corresponds to ions with a mass of four experiencing approximately 26 cycles of the ac field, the mass peak obtained is shown in Fig. 7. Figure 8 shows a sequence of ''*contour*'' maps that indicate where the ions transmitted by the filter originated in the ion source. The maps, marked a to f in Fig. 8, are drawn to correspond to the labeled points in Fig. 7. Ions originate with equal probability at all points in the source which is represented by the circle. The solid area inside the circles shows the area of the source from which the majority of those ions that reached the detector originated. The solid areas were determined by dividing the source into small areas and finding the number of ions that reached the detector for each area. The area with peak intensity was found for each map and a smoothed contour drawn through those areas whose count number was 20% of the peak value. Contour smoothing is necessary because the number of ions in each source elementary area is relatively small; statistical fluctuations produce random variations that are not a function of the system behavior. The contour maps show that on the low mass side of the peak (ions trajectories are stable in the x direction) ions originate close to the x axis. On the high mass side (trajectories stable in the y direction) ions originate close to the y axis. Results close to the peak indicate that ions originate with no bias towards proximity to a particular axis in the source plane.

Regardless of point of origin, detailed examination of the

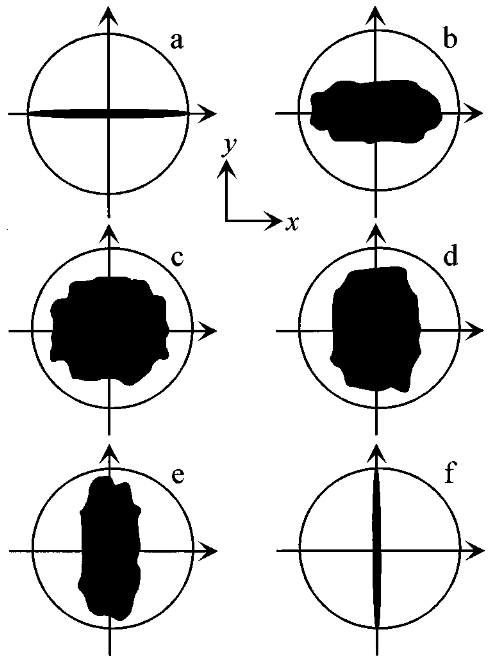

FIG. 8. *Contour* maps indicating the regions of the ion source where ions transmitted by the quadrupole originated.

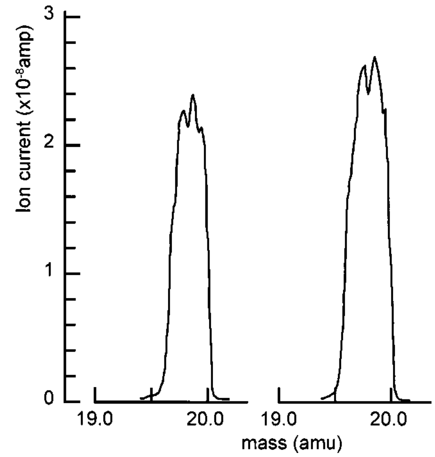

FIG. 9. Experimental observations of an Ar^{++} mass peak at two resolution settings exhibiting peak splitting.

results indicates that ions originating close to the filter axis are more likely to be transmitted than ions originating at a distance from the axis. This greater transmission of ions originating close to the axis was indicated in the earlier article by Voo *et al.*[4] but the directional effects can only be observed by using a large number of ions spread uniformly over the source.

These results provide an explanation for the results shown in Figs. 2 and 3. Ions originating close to the filter axis have a much higher probability of reaching the detector than ions starting at a distance from the axis. Using uniform source illumination and increasing the ion source diameter while retaining the same total number of ions (constant ion current but varying ion current density) reduces the number of ions that reach the detector. This is because a larger proportion of the ions originates at a large distance from the axis in the low current density case than in the high current density case. Additionally the bias towards the x or y axis, when not at the peak, affects the behavior in a complex manner and causes the peak shape to vary as the source size changes.

E. Effects of the exit aperture

As modifications to the source were found to affect the performance predicted it was thought that alterations to the exit aperture might also affect the behavior of the filter. For all results presented so far the only ions rejected were those considered to strike the rods. This was defined to occur when the magnitude of either the x or y coordinate of the ion exceeded the quadrupole radius, r_0. This is equivalent to the use of a very large exit aperture or defining the exit aperture to be a square of side $2r_0$; this is also the method adopted by other authors.[1]

When the exit aperture was changed to a circular one of radius r_0 there was little effect but as the aperture radius was reduced structure was observed in the mass peaks. Such structure has been observed in practice; Figure 9 shows two experimental measurements of a mass 20 peak at different resolutions. Structure is clearly seen, features occur at approximately the same points on the mass scale but, because the resolution is different, it is not immediately apparent that the structural features occur at approximately the same position on the mass scale each time.

An example of structures produced by the computer model is given in Fig. 10. The model is set to give approximately the conditions used for the lower resolution experimental results in Fig. 9. The peaks were obtained using a source radius of $\frac{1}{4}r_0$ with the exit apertures increasing from left to right in the figure. The first peak is for an exit radius of $\frac{1}{2}r_0$, the second for $\frac{2}{3}r_0$, and the third unlimited (as earlier a square of side $2r_0$). It appears that the amplitude of the structure depends on the exit radius.

So far our investigations have not found sufficient correlation between changes in specific quadrupole parameters

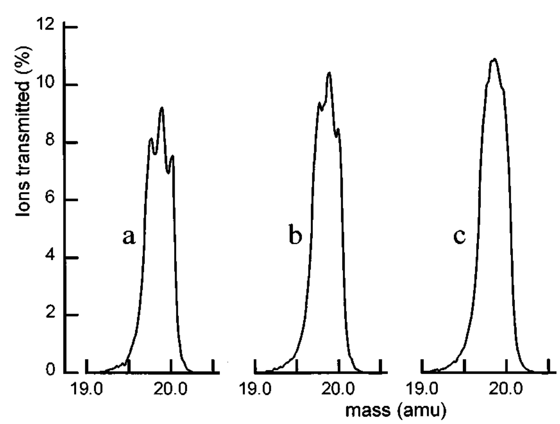

FIG. 10. Computed mass peaks for Ar^{++} with the exit radius of the quadrupole increasing from left to right; (a) $\frac{1}{2}r_0$, (b) $\frac{2}{3}r_0$, and (c) unlimited, equivalent to a square of side $2r_0$.

and their effects on peak structure to enable us to predict which parameters must be altered to produce a particular experimentally observed structure.

IV. CONCLUSIONS

Using the improved model of the quadrupole mass filter with ion source effects incorporated it has been possible to simulate the behavior of a quadrupole mass filter for a wide range of conditions. The general form of results shows many areas in which there is excellent agreement between the computations and experiment. Many of the effects observed experimentally are seen and, in most cases, the model provides indications of which parameters of the instrument must be adjusted to cause specific effects.

With the present model the exact shape and height of experimentally obtained mass peaks are not always reproduced. However, it has been shown that relatively small changes in the way the ion source and detector are modeled can significantly change peak shape and height. Although shape and height change with ion source model the peak width does not vary significantly. Consequently, we have suggested that graphs to illustrate quadrupole resolution (peak width) should be drawn using the parameter η instead of the peak height.

It is recognized that the present version of the model lacks a number of features. It should be relatively simple to include a spread in the ion energy. It should also be possible to add a spread in the direction in which ions enter the filter although, as this removes the assumption that $v_x = v_y = 0$, the program code will require greater changes to implement this. Further, as these additions add more randomly selected parameters to the model the number of ions passed through the filter must be increased to avoid large uncertainties in the results.

The effect of the exit radius on the peak structure adds to evidence that the entry and exit conditions strongly influence quadrupole performance. Similar effects are caused by fringe fields between the rod system and the ion source and ion detector. These are known[1] to have a significant effect and efforts are in progress to add these to the model.

As ion source behavior has been shown to strongly influence quadrupole operation it is intended to separate the ion source simulation and quadrupole filter parts of the simulation program. It will then be possible to combine results of separately developed ion source simulation programs with the quadrupole simulation.

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[7] Contact the authors at the address given for copies of the program.