Transmission through the quadrupole mass spectrometer mass filter: The effect of aperture and harmonics

A. C. C. Voo, R. Ng,[a] J. J. Tunstall,[b] and S. Taylor
Department of Electrical and Electronic Engineering, University of Liverpool, Brownlow Hill, Liverpool L69 3BX, United Kingdom

(Received 18 July 1996; accepted 14 February 1997)

This article considers the effect of initial ion energy and quadrupole rod length on transmission percentage of ions through the mass filter for a computer simulation of the quadrupole mass analyzer. It also examines the effect of aperture for the mass filter with sinusoidal rf ac and rf ac with harmonics. © *1997 American Vacuum Society.* [S0734-2101(97)03904-3]

I. INTRODUCTION

Quadrupole mass spectrometers (QMSs) are widely used in both industry and research for fast accurate analysis of gas and vapors. An example of how a QMS may be used is in a semiconductor fabrication plant as a residual gas analyzer. A description of the QMS and its operation is available in the scientific literature[1,2] and is not repeated here. The QMS contains basically three elements; (i) ion source, (ii) mass filter, and (iii) ion detector. Much experimental work is reported[3] but very little has been written on the modeling of the mass filter.

Ma and Taylor[4] provided a Turbo-PASCAL program for solving the Mathieu equation in two dimensions for a finite quadrupole mass filter. The program runs under DOS on a PC and is available from the authors.[5] It includes error handling and data handling routines. The program can be divided into three parts:

(i) ion trajectory determination,
(ii) generation of a stability diagram, and
(iii) transmission analysis.

Each of the three options work independently. The program uses a fourth-order Runge–Kutta numerical approximation to solve the Mathieu equation. The effect of rf magnitude and initial phase angle of the alternating voltage on ion transmission through the mass filter were studied. The geometry of the quadrupole, i.e., x, y, z directions and aperture angles, are defined in Fig. 1. Calculation of ion transmission by successive determination of ion trajectories in the x and y directions was examined. The rf phase angle was varied in one degree steps over the range 0°–360°. The percentage transmission in the x and y directions, i.e., distance traveled along the filter in percent for the varying phase was calculated using the program. The results show the following:

(i) Ion transmission probability depends upon the phase of the rf wave form at the time of injection into the QMS mass filter.
(ii) Radio frequency phase has a greater effect upon ion trajectory in one direction than in the other.
(iii) Ions injected at different values of rf phase which are unstable and not transmitted through the mass filter are not all equally unstable. The implication is that shorter mass filters, smaller N (where N is the number of rf voltage cycles applied to the quadruple lens), may allow ions to be transmitted which for a longer filter, larger N, would be outside the stability region [see Eq. (9)].

A simulated mass spectrum of 100 ions with mass 28 amu, the rf varying between 120 and 124 V in 200 mV increments, for a fixed ratio of direct to alternating voltage, predicts a mass peak at 122 V. There was sharp drop on the high mass side of the peak and a long tail on the low mass side. This result is repeated experimentally and so cannot be an artefact. Ma and Taylor studied the effect of different length mass filters. They found that as the effective length of the quadrupole increased the resolution of the mass peak improved and for $N > 200$ [see Eq. (9)] the results are indistinguishable from a mass filter where N tends towards infinity.

In this article we investigate more aspects of the program developed and look at the dependence of the percentage transmission of ions on initial ion energy and quadrupole rod length. Dawson[6] considered aperture sizes for the mass filter and examined the dependence of transmission percentage as a function of initial phase angle. A matrix technique was used to solve the Mathieu equation for an infinitely long filter. In this article aperture angle will be examined. Ions will be considered moving with initial velocities parallel to the axis of the mass filter. Dawson summed his transmission of ions through these aperture angles, whereas we shall consider percentage transmission over all possible phase angles for fixed entrance aperture angles. Considered also is the effect of increasing the harmonic content of the rf wave form. Harmonics are present in all experimental wave forms. The higher frequency content is of particular interest especially with square waves for operation of high frequency miniature quadrupole mass filters.[7] Using Fourier series, the program described in Ref. 4 has been modified to allow ion trajectory simulation for excitation of the mass filter by sinusoids of varying frequency and amplitude.

[a]School of Combined Engineering, Liverpool University, UK.
[b]Author to whom correspondence should be addressed; Electronic mail: ee63@liv.ac.uk

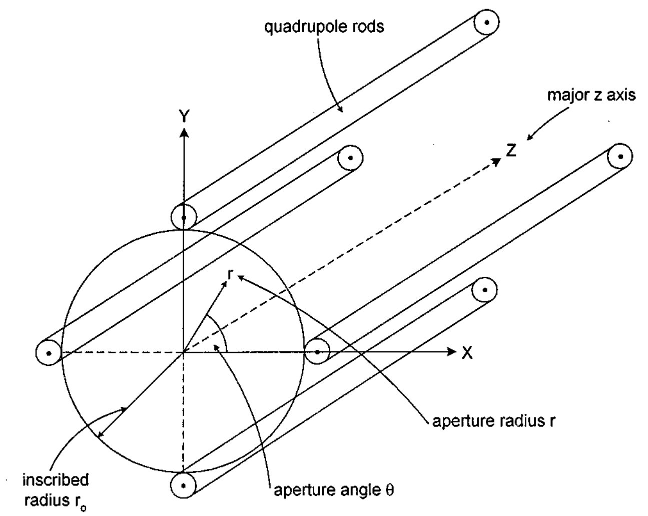

FIG. 1. This diagram shows the geometry of the ideal quadrupole mass filter. The aperture radius and the aperture angle are measured in the $x-y$ plane. The z axis is the major axis of the mass lens.

II. BACKGROUND THEORY

The mass filter of the QMS selects ions with certain charge to mass ratios through the application of direct and alternating electromagnetic fields to the electrodes of the mass spectrometer. For given values of these fields ions will either pass through the filter or will collide with the rods of the quadrupole, giving a charge to the mass selection system for the ions. The electrodes of the quadrupole mass filter are in general assumed to be hyperbolic though in real analyzers cylindrical rods are often used. The potential distribution in the ideal mass filter is given by

$$\phi(x,y,z)=\phi_0\frac{x^2-y^2}{2r_0^2}, \tag{1}$$

where x and y are the directions defined in Fig. 1 and r_0 is the inscribed radius of the filter. This potential satisfies Laplace's equation and is invariant in the z direction, the major axis of the mass filter.

Consider next the motion of an ion, with charge e and mass m under the influence of a time varying potential ϕ_0, in the x and y directions. For the ideal mass filter operation a combination of direct (U) and alternating voltages (V) is chosen and applied to opposite rods such that

$$\phi_0=U-V\cos(2\pi ft), \tag{2}$$

where f is the frequency of the rf voltage. Thus the equations of motion in the $x,y,$ and z directions are

$$\frac{d^2x}{dt^2}+\left(\frac{e}{mr_0^2}\right)(U-V\cos\omega t)x=0, \tag{3}$$

$$\frac{d^2y}{dt^2}-\left(\frac{e}{mr_0^2}\right)(U-V\cos\omega t)y=0, \tag{4}$$

$$\frac{d^2z}{dt^2}=0, \tag{5}$$

$$a_u=a_x=-a_y=\frac{4eU}{m\omega^2r_0^2}, \tag{6}$$

$$q_u=q_x=-q_y=\frac{2eV}{m\omega^2r_0^2}. \tag{7}$$

Equations (3) and (4), with $\xi=\omega t/2$, can be rewritten as the general form of the Mathieu equation,

$$\frac{d^2u}{d\xi^2}+(a_u-2q_u\cos 2\xi)u=0. \tag{8}$$

We can see from Eq. (8) that the trajectory of the ion depends on the phase angle ξ at which the ion enters the analyzer. Solution of Eq. (8), for suitable boundary conditions exactly determines the path the ion takes through the ideal quadrupole. Analytic solutions to Eq. (8) exist for an infinite length mass filter. Solving Eq. (8) for finite length quadrupole requires a numerical solution.

The effective ''length'' of the quadrupole analyzer is given by the number of rf cycles experienced by the ion during its transit through the analyzer. This is given by

$$N=\frac{fl}{v_z}, \tag{9}$$

where f is the frequency of the rf voltage, l is the length of the quadrupole rods, and v_z is the initial velocity of the ion in the z direction. If the ion experiences an obstruction-free path over the defined N, it is said to be stable within this length. Conversely, an ion that is unstable strikes the rods of the mass filter.

III. RESULTS: THE EFFECT OF INITIAL ION ENERGY AND ANALYZER LENGTH ON TRANSMISSION

The effect of initial ion energy on the percentage transmission of ions was studied through the simulated quadrupole analyzer. The effective length N appears as a parameter in the program simulation and, as stated earlier, depends upon initial ion velocity, frequency of the rf applied to the rods, and the quadrupole mass analyzer length. The initial energy of the ion can be varied through N since the kinetic energy has a direct relationship with the velocity of the ion as given by Eq. (10).

The input energy of the ion is given by the nonrelativistic form for the kinetic energy E_0,

$$E_0=\frac{1}{2}mv_z^2=\frac{1}{2}m\left(\frac{fl}{N}\right)^2, \tag{10}$$

where m equals the mass of the ion and v_z is the velocity of the ion initially in the z direction. The initial velocity of the ion in the x and y directions was taken to be zero.

The simulation was run for 360 N_2^+ ions with a phase angle starting at 0° and incrementing by 1° for each cycle. The initial energy was varied through N, the effective number of rf cycles applied to the rods of the quadrupole. The coordinates for the ion were 0.3 mm in the x direction and

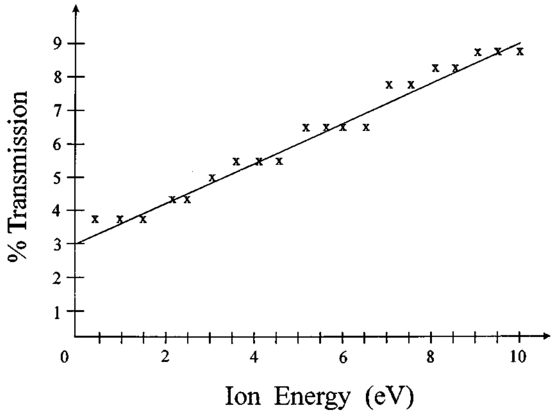

FIG. 2. The simulated percentage transmission of ions through the mass filter is shown plotted against initial ion energy measured in electron volts. The dc supply to the quadrupole rods was taken to be 20.5 V and the amplitude of the rf voltage was set at 123.5 V with a frequency of 2 MHz. The coordinates for the ion injection were 0.3 mm in the x direction and 0.3 mm in the y direction. The inscribed field radius r_0 within the mass filter rods was taken to be 2.75 mm.

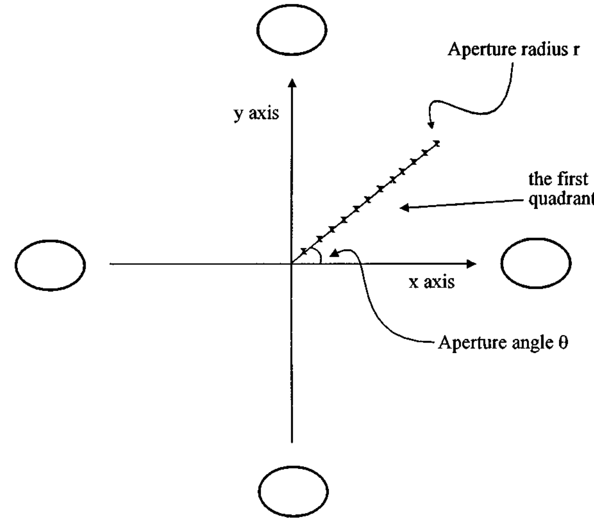

FIG. 4. This figure illustrates how the aperture angle θ is measured. The diagram is a cross section of the mass filter. The z axis of the quadrupole is perpendicular to the plane of the paper.

0.3 mm in the y direction. The inscribed field radius r_0 within the quadrupole rods was taken to be 2.75 mm.

As N was varied it was shown by the simulation results that ions with larger initial energy have a higher probability of passing through the mass filter undeflected. Figure 2 shows the percentage of ions traversing the analyzer against initial ion energy and illustrates this point.

To vary the length of the quadrupole rods in the simulation requires us to again change the value of N, the number of rf cycles applied to the analyzer. Equation (9) shows how N varies with l, the quadrupole rod length. Figure 3 shows the transmission percentage of nitrogen ions N_2^+ for initial energies of 1 and 2 eV with the variation of the length of the quadrupole rods. All other parameters in the simulation were kept the same, as for Fig. 2. Figure 3 illustrates that the percentage ion transmission decreases for a longer quadrupole rod analyzer length.

After running the simulation it was found that nitrogen gas ions passed through the mass filter only with phase angles around 90° and 270°. This is important in the design of a QMS. In the case of nitrogen ions preferentially injected into the mass filter at phase angles 90° and 270° of the rf supply, this would lead to maximum transmission characteristics of the instrument.

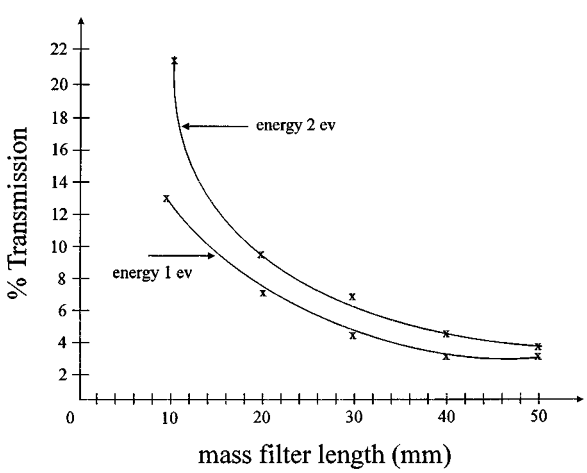

FIG. 3. The simulated percentage transmission of ions through the mass filter is shown plotted against quadrupole rod length for ions with initial energy of 1 and 2 eV, respectively. The dc supply to the mass filter was taken to be 20.5 V and the amplitude of the rf voltage was set at 123.5 V with a frequency of 2 MHz, as in Fig. 1. Again the injection points of the ions was taken to be 0.3 mm in the x direction and 0.3 mm in the y direction. The inscribed field radius r_0 was 2.75 mm.

IV. INVESTIGATION OF THE APERTURE ON TRANSMISSION PROBABILITY

A. Sinusoidal wave forms

The variation of aperture on the transmission probability will be considered for a rf voltage which is sinusoidal (the usual case). The aperture angle is measured from the x axis as shown in Fig. 4.

The voltage conditions and the frequency of the rf potential remained the same. The velocity of the ions in the x and y directions was initially taken to be zero. N was fixed at 38 and the point of injection varied. Cylindrical polar coordinates (r,θ,z) were used to parameterize the variation of the injection position of the ion. In Fig. 5 the plot shows percentage transmission of ions against the point of injection, i.e., aperture radius r and aperture angle θ. The initial position of the ion on the z axis (the axis of the mass filter), was taken to be zero. As r increases from 0.9 to 2.5 mm, percentage transmission falls for each aperture angle. For fixed r the percentage transmission was found to be the same for θ=0°, 45°, 135°, 180°, 225°, and 315° (group A in Fig. 5). This is shown as one curve. In addition at θ=90° and 270°, the

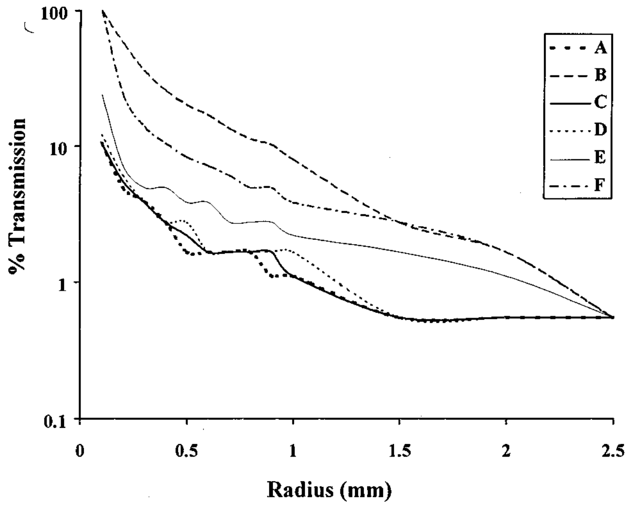

FIG. 5. The figure shows the simulated percentage of ions successfully transmitted, plotted against aperture radius. The curves are labeled A–F and for certain aperture angles, the plots are coincident. Group A represents coincident curves for the following aperture angles: 0°, 45°, 135°, 180°, 225°, and 315°. Group B represents coincident curves for aperture angles: 90° and 270°. Group C represents an aperture angle of 15°. Group D represents an aperture angle of 30°. Group E represents an aperture angle of 60°. Group F represents an aperture angle of 75°.

percentage transmission was also the same, for fixed r (group B in Fig. 5). This again is shown as one curve.

Injection angles of $\theta=15°$, 30°, 60°, and 75° were also investigated, curves C–F in Fig. 5 show the results. The coincident aperture angle curves reveal symmetries of the system. It is clear that only the first quadrant of the mass filter need to be examined for transmission probability. It should be noted that 100% transmission occurs only when 360 nitrogen ions have passed successfully in the simulation. Usually the number of ions which is transmitted is less than this.

To summarize, the results of the entrance aperture conditions on percentage transmission of ions in the simulation shows the following:

(i) Ion transmission characteristics are symmetrical about the x and y axes.
(ii) The percentage transmission is larger if the aperture radius r is small, i.e., closer to the z axis, as opposed to injection coordinates further away from the center.
(iii) At aperture angle 90° (or 270°), and a radius of 0.1 mm, 100% of the ions were transmitted through the simulated mass filter.

The aperture angles are important to the design of future QMSs. A lens system might be constructed so that the ions could be injected into the mass filter at certain aperture angles to give maximum transmission characteristics.

The next point that will be considered is the addition of harmonics to the rf component applied to the quadrupole rods in the simulation. This will be examined in Sec. IV B.

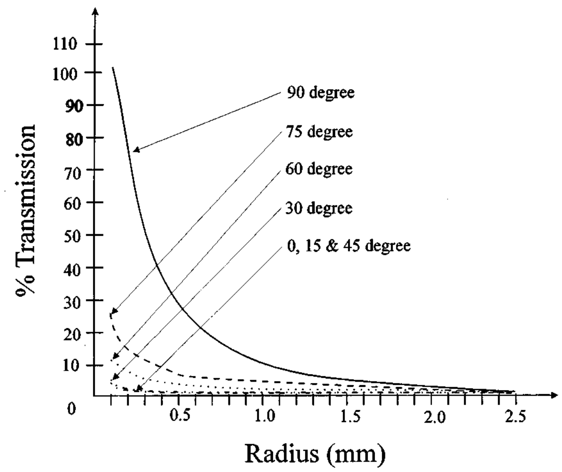

FIG. 6. The simulated percentage of ions transmitted through the mass filter is plotted against the aperture radius. The series of curves shows the variation of transmission percentage with aperture angle.

B. Addition of harmonics

An interesting variation of using sinusoidal voltage is to use square wave rf on the quadrupole rods. This can be modeled simply by replacing the sine wave component of Eq. (2) by a Fourier expansion of the rectangular wave form according to Eq. (11)

$$F(t)=\frac{4}{\pi}[\sin 2\pi ft+\tfrac{1}{3}\sin 2\pi(3ft)+\tfrac{1}{5}\sin 2\pi(5ft)+\cdots]. \quad (11)$$

The dc potential is still assumed to be applied to the quadrupole system. This will naturally add harmonics to the system since at some point it will be necessary to truncate the expression. Expanding the square wave one notices that only odd number harmonics enter the series. To simulate the mass filter with square wave rf we included a certain number of harmonics entering the differential equation. The differential equation can again be solved numerically using fourth-order Runge–Kutta. It is instructive to compare the effect of using harmonics in the rf wave form with the pure sine wave. First it is necessary to look at the comparison on the effect of the aperture using the harmonic approximation to the rectangular wave form.

For sine wave with the third harmonic the first key feature is that for aperture angles 0°, 15°, and 45° the transmission percentage of ions is the same. In Fig. 6 the results for 30°, 60°, 75°, and 90° are shown along with the coincident curves for 0°, 15°, and 45°.

The curves shown follow approximately an inverse square law. At 90° maximum transmission is achieved with the minimum for 0°, 15°, and 45°. For aperture angle 75°, a comparison between the various orders of harmonics from third up to seventh inclusive was made. A plot of this is given in Fig. 7.

The sensitivity goes down as more harmonics are added compared with the sine wave (given in Fig. 8), the decrease in sensitivity is quite dramatic. However, a comparison be-

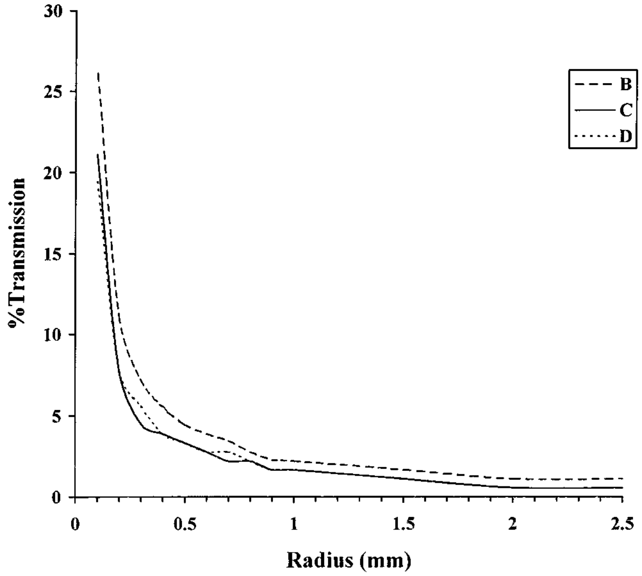

FIG. 7. Simulated percentage transmission of ions is plotted against aperture radius for various harmonic inclusions. The curves show the effect of using increasingly more accurate approximations to the square wave rf voltage applied to the mass filter rods. Curve B shows the sine wave rf with the third harmonic. Curve C shows the sine wave rf with the third and fifth harmonics. Curve D shows the sine wave rf with the third, fifth, and seventh harmonics.

tween the percentage transmission against aperture radius for approximate square wave excitation of the mass filter at an aperture angle of 75° with the sinusoidal rf at 30° shows a slightly better performance in the sensitivity of the square wave. This is illustrated in Fig. 9.

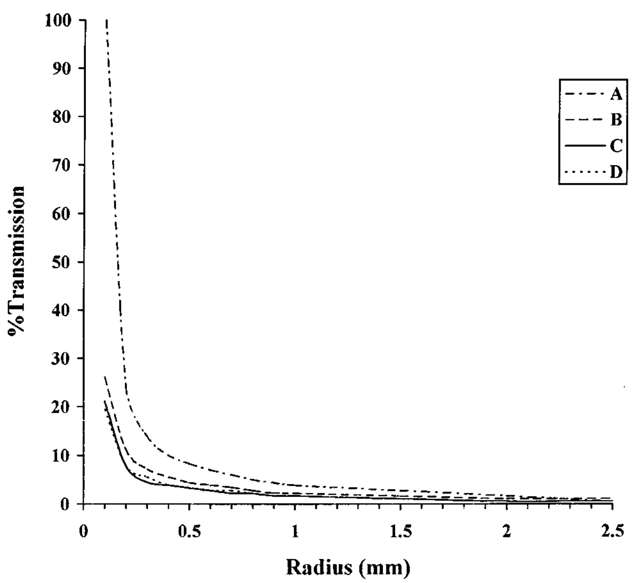

FIG. 8. The curves shown illustrate the difference between the sinusoidal rf voltage and the square wave approximation on the simulated transmission percentage vs aperture radius. The aperture angle was taken to be 75°. Curve A shows the pure sine wave rf. Curve B shows the sine wave rf with the third harmonic. Curve C shows the sine wave rf with the third and fifth harmonics. Curve D shows the sine wave rf with the third, fifth, and seventh harmonics.

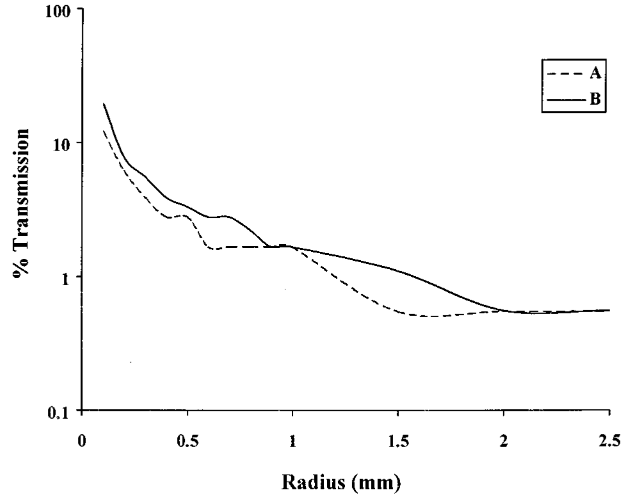

FIG. 9. The plots show the simulated percentage transmission against aperture radius for ions injected at aperture angle 30° in curve A with sinusoidal rf and ions injected at 75° in curve B with approximate square wave rf (sine wave with the third, fifth, and seventh harmonics).

V. SUMMARY OF THE RESULTS

The simulation results indicate that ions with larger initial velocity or energy have a higher probability of passing through the quadrupole. Ions which pass through a shorter mass filter have a higher percentage transmission as compared with a longer quadrupole. Both investigations show that the smaller the time the ions spent in the analyzer, the greater the probability of transmission. In the aperture studies, the closer an ion is injected to the center of the axis of the electromagnetic field, the greater the probability of the ion passing through the quadrupole. Maximum transmission of ions occurred for aperture angles of 90° and 270°. The addition of harmonics to the rf voltage in the form of a Fourier expanded square wave gives a reduced sensitivity in the operation of the simulated mass filter compared with the usual sinusoidal wave form. For comparisons of certain different aperture angles it has been shown that the mass filter is more sensitive to square wave excitation than to sine wave rf voltage. However, it is clearly seen that there is a possibility of operating the QMS with rectangular wave forms as opposed to sine wave rf voltage. This may be particularly advantageous when high frequency miniature quadrupoles are used. In this case, the generation of high frequency square wave forms using application specific integrated electronics in the proximity of the QMS mass filter would be possible with an associated reduction in cost and improvement in reliability.

ACKNOWLEDGMENTS

The authors would like to thank Professor J. H. Leck and the late W. E. Austin for many stimulating discussions and the EPSRC for the funding of this project.

[1]F. M. Mao and J. H. Leck, Vacuum **37**, 669 (1987)
[2]P. H. Dawson, *Quadrupole Mass Spectrometry and its Applications* (Elsevier, New York, 1976).
[3]J. H. Batey, Vacuum **37**, 659 (1987).
[4]F. M. Ma and S. Taylor, IEEE Proc. Sci. Meas. Technol. **143**, 71 (1996).
[5]Please contact Dr. S. Taylor at the address in this article if you require a copy of the program and supporting documentation.
[6]P. H. Dawson, Int. J. Mass Spectrom. Ion Phys. **14**, 317 (1974).
[7]R. J. Ferran, US Patent No. 5,401,962 (1995).