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Asymmetrical features of mass spectral peaks produced by quadrupole mass filters

John Raymond Gibson* and Stephen Taylor
The Department of Electrical Engineering and Electronics, The University of Liverpool, Brownlow Hill, Liverpool L69 3GJ, UK

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The individual mass spectral peaks produced by a quadrupole mass spectrometer (QMS) are asymmetric; they exhibit a 'tail' on the low mass side. In some cases a definite structure is observed in the tail. We show that the tail structure is a consequence of the use of circular electrodes. An extreme case of an experimentally observed QMS mass peak with a distinct tail structure is shown and the general form is reproduced using our numerical model. The effect of instrument resolution, length, operating frequency, ion energy, mass and ion source aperture upon the tail structure are considered. Results show that extensive long tails originate mainly from ions that enter the mass filter at a relatively large distance from the QMS axis; also no significant tail is produced in the case of ideal hyperbolic form electrodes of finite length. Copyright © 2003 John Wiley & Sons, Ltd.

One feature of a quadrupole mass spectrometer (QMS) is that the shape of the mass peak is often asymmetrical.[1–3] This occurs for instruments constructed with either hyperbolic or circular section electrodes (rods). Asymmetry may be increased by manufacturing imperfections and is also affected by fringe fields at the ion entrance and exit positions.[4] Manufacturing considerations are such that most commercial instruments use circular cross-section rods rather than hyperbolic cross-section ones; this usually increases the asymmetry as well as reducing the peak height and resolution for similar operating conditions. Features of the ion source may also affect the peak shape.

Our previous work[5,6] predicted behaviour of QMS systems with circular cross-section rods using numerical modelling techniques. Conventionally, the rod radius is denoted by r and the rod separation is defined using r_0 as the radius of the inscribed circle that just touches the rods. Performance depends on the dimensionless quantity r/r_0 and the earlier predictions[6] suggested that the optimum value of r/r_0 was lower than the range 1.148 down to 1.14511 predicted[7–10] by analytical treatments. The optimum value from our model varied slightly as instrument parameters were changed but was usually between 1.125 and 1.13; several commercial instruments use values in this range. The previous analytical techniques assumed that ideal operation occurs when the first term in the harmonic expansion of the field is zero; we suggested[6] that the ideal operation would occur at some point when several terms combine to produce the optimum performance. This has recently been confirmed by an analytical approach[11] that examined the effect of several terms in the harmonic expansion and obtained an optimal value for r/r_0 in the range 1.128 to 1.130.

**Correspondence to*: J. R. Gibson, The Department of Electrical Engineering and Electronics, The University of Liverpool, Brownlow Hill, Liverpool L69 3GJ, UK.
E-mail: jrgjrg@liv.ac.uk

Both the analytical approach[11] and our computations[6] for round rods showed significant tails on the low mass side of the peak, with larger tails produced by our computations. The magnitude and mass range over which the tail is apparent varied with both r/r_0 and with the setting of the resolution control. In general the magnitude of the tail decreases as r/r_0 decreases. That is, the tail is less pronounced at the suggested lower r/r_0 value than at higher values around 1.146. The tail continues to decrease as the ratio is reduced below 1.125, although the resolution starts to deteriorate. When a hyperbolic field is used no significant tail is observed. Figure 1 shows typical computed spectra for round rods with r/r_0 values of 1.127 and 1.146, and for hyperbolic rods ($r_0 = 2.76\,\text{mm}$, rod length 127 mm, operating frequency 8 MHz, ion energy 2 eV, resolution control setting $\eta = 0.9991$ where η is defined later). The peaks shown have been normalised to be equal in magnitude and in position of the peak centre at 50% of the height because both magnitude and position change as the rod form is changed. We have now investigated the tail in more detail.

EXPERIMENTAL

The late W. E. Austin performed an extensive series of very detailed experiments at the University of Liverpool on the behaviour of a typical QMS system designed to operate with resolution in the range 200–500 (here defined as the mass of the ion divided by the peak width at 10% of peak height; some authors define resolution using the width at 50% of the peak height). Most results were not published because detailed features of the observations could not be fully explained. Many of Austin's investigations used the rare gases as the sample material because single well-resolved mass peaks are obtained even at low-resolution settings. Some, but not all, of the measurements show a low mass tail. When the tail is examined with sufficient gain it

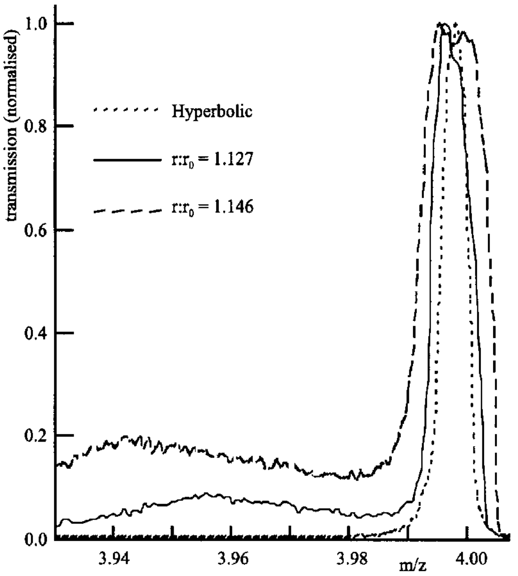

Figure 1. Typical mass peak shapes computed for different geometry QMS systems (normalised to the same height and mass position).

can appear in a number of forms; the most extreme found was a broad low amplitude feature with a slight peak with an amplitude of about 0.001–0.002 of that of the main peak. Even when present such a tail is not always observed, since typical QMS operation displays complete mass peaks and the tail is too small to be observed; often the magnitude of the tail is similar to the noise level.

One of the spectra for the ion $[^4He]^+$ observed by Austin is shown in Fig. 2(a); the regions on the high and low mass sides of the peak are also shown magnified a hundred times. Our computed spectrum (Fig. 2(b)) for a similar specification QMS system ($r/r_0 = 1.127$ and other parameters as given in Fig. 1) is shown alongside the experimental results but the magnified version is only four times the original. The resolution control setting, η, was set to 0.9991 as this best matches the observations ($\eta = U/V$, the ratio of the DC amplitude to the AC amplitude and $\eta = 1$ corresponds to the peak of the stability diagram for hyperbolic section electrodes). The model produces a larger tail than is observed but it is of similar shape to the experimental one and the secondary peak is at approximately the same position relative to the main peak. The origins of the mass scales differ because the scale for the experimental measurements is determined by calibration using a known gas mixture. The scale for the model is determined by setting the mass scale from the amplitude of the applied radiofrequency (RF) voltage such that the peak of the stability diagram, when hyperbolic section electrodes are used, determines the mass value. Using this voltage-based calibration causes the main peak for the computed results to be at a position that is lower than the true mass.

The shape of the tail was found to vary with several parameters; we have investigated effects that cause the model to produce differences in the low mass tail. As indicated above the tail changes with the value of r/r_0 selected. In general, when other parameters are varied, changes in amplitude and shape of the low mass tail vary for different values of r/r_0, but the nature of changes (trends) are the same for all the values of r/r_0 investigated. The detailed results presented here for investigations of the model behaviour with other parameters are for $r/r_0 = 1.127$, as this is close to the optimum value suggested previously[6,11] and is used by some manufacturers.

Effect of resolution control setting

A QMS instrument may be used to perform a mass scan at constant resolution (ion mass divided by peak width), or at constant peak width where the resolution varies with ion mass. For most experimental applications constant peak width is preferred. However, when investigating the effect of adjusting construction and operating parameters, by examining a single mass peak as the parameters are changed, it is more convenient to operate in the constant resolution

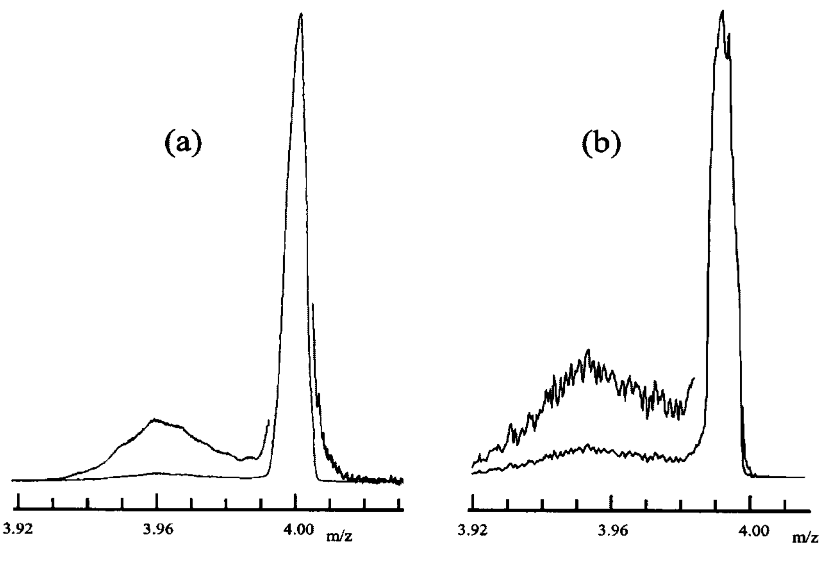

Figure 2. Experimental observations (a) and computations (b) of $[^4He]^+$ mass spectra exhibiting a significant low mass tail. Magnified regions are ×100 in (a) but only ×4 in (b).

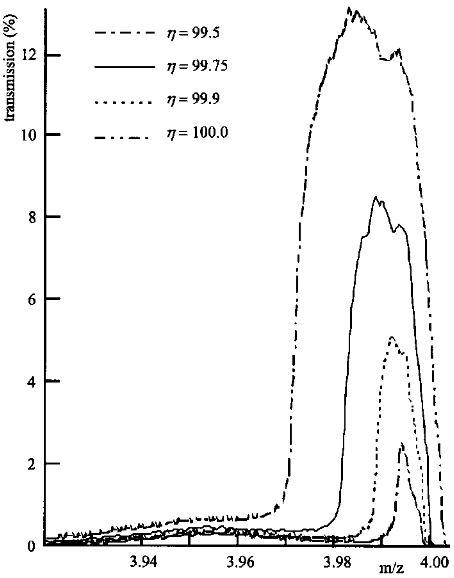

Figure 3. Mass peak shapes at different resolution control settings for a round rod QMS.

mode. To scan at constant resolution the ratio of the magnitudes of the applied DC and AC voltages is maintained constant while their absolute values are increased. The resolution setting is controlled by adjusting the ratio of the two voltages, U and V, and the setting of the resolution control is described by the parameter $\eta = U/V$ defined earlier. As η is increased the heights of the main peak and the low mass tail both decrease and the main peak width also decreases. The main peak width decreases more rapidly than the height, thus improving the resolution up to a limit;[5] the resolution limit depends on a number of design and operating features.

Figure 3 shows computed peaks for a number of resolution control settings, η, for the QMS system used to produce the results in Fig. 2. At low values of η the low mass side of the main peak and the low mass tail merge and it is difficult to separate the two features. As the resolution control setting is increased the low mass tail separates and the tail appears to vary less with the setting than the main peak. This is confirmed by Fig. 4, which shows the heights of the main peak and that of the separated low mass tail as a function of the resolution control setting. Both heights have been normalised to unity at $\eta = 0.997$, the lowest value at which the two effects can be well separated. Uncertainties shown for the low mass tail results reflect statistical fluctuations because the number of ions transmitted is very small (less than 0.5% of the 10^5 ions injected). The model indicates that the low mass tail amplitude does not decrease as rapidly as the height of the main mass peak as the resolution control setting is increased. The tail continues to be present at control settings well above those at which the main peak no longer exists.

Effects of quadrupole length, frequency, ion energy and ion mass

The QMS filter action depends on the number of cycles of the RF field experienced by ions as they travel through the filter. This number can be adjusted by changing either the length of the filter, or the frequency of the RF field, or the energy of the

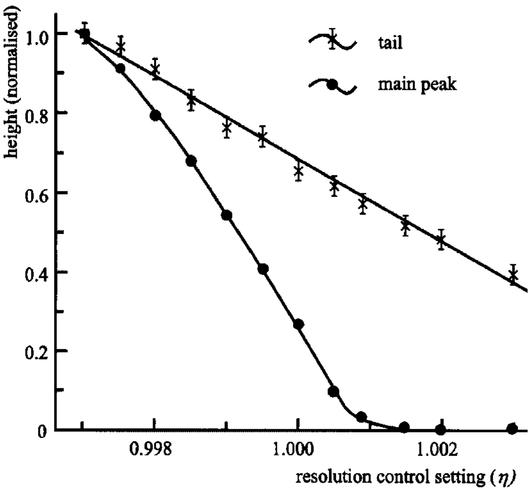

Figure 4. Variation of the main and tail peak heights with resolution control setting (normalised to unity at $\eta = 0 \cdot 997$).

ions (velocity in the axial direction). As the number of cycles increases for a fixed resolution control setting, the shape of the main peak becomes more distinct and the height is reduced to some extent. In particular, as the number of cycles increases both sides of the peak become more clearly defined and the height of the low mass tail decreases.

For the results shown in Figs. 2 and 3 at a frequency of 8 MHz the mass 4 ions experience about 100 cycles of the field. Figure 5 shows the effect of lower and higher numbers of cycles. Adjusting the length, frequency and ion energy such that the number of cycles experienced by the ions stays constant has no effect on either the main peak (this is known to be true for hyperbolic section rods as the behaviour can be expressed in analytical form) or the low mass tail. This indicates that the motion of the ions producing the low mass tail is not dependent on the absolute ion velocity in the direction of the QMS axis (this can be regarded as ion energy as in most QMS applications the ions are injected in the axial direction with only small transverse velocity components).

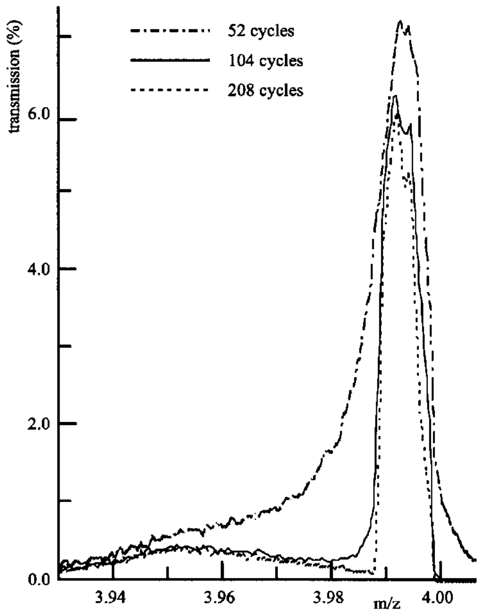

Figure 5. Mass peak shape variation for different numbers of cycles of the RF field experienced by ions.

A relatively low number of cycles, typically about 80, is required to obtain a well-defined main peak. However, the base of the main peak and clear peak formation of the low mass tail become more distinct as the number of cycles is increased to over 200. If the ion source is operated such that ions are extracted with constant energy then the axial velocity falls as the mass rises. Hence for constant resolution operation peaks become better defined at higher masses. By adjusting the ion energy as the mass was varied, so that the number of cycles experienced by ions remained constant, we determined that the form of the low mass tail is not affected by the ion mass.

Effect of the ion source

The results in Figs. 1–5 were obtained using a simple ion source model. The ion source is assumed to be a circular disc with the QMS axis passing normally through the centre of the disc. Ions are generated in equal numbers at all points in the disc (i.e., the ion source is uniformly illuminated) and the disc radius is $0.18 \times r_0$. All ions leave the source in the direction parallel to the axis of the QMS system. In an earlier paper[12] we showed that for finite length ideal hyperbolic section electrodes, the transmission of ions of a particular mass through a QMS at different points on the mass scale depends on the position of ions when leaving the ion source. Using circular section electrodes the effect of ion entry position is similar for the main peak, but behaviour for the low mass tail is unknown.

In general a QMS instrument transmits more of the ions that originate close to the axis than it does those that originate a distance from it. Hence, if a uniformly illuminated ion source is used and the total ion current is maintained constant, the peak height reduces as the source radius is increased. Figure 6 shows the results for sources with three radii; these have been normalised to the same peak height of 1.0 and the scale expanded to show the tail region clearly. It is apparent that the ion source radius affects the behaviour of the low mass tail. If the ion source radius is above about $0.15 \times r_0$ the tail shape is constant but its maximum height as a proportion of the main peak height decreases as the radius increases. This suggests that the ions contributing to the tail originate in a particular region of the source entirely within the $0.15 \times r_0$ radius. As the radius increases further this region becomes a smaller fraction of the source and normalisation reduces the apparent height. When the source radius is reduced to slightly below $0.15 \times r_0$, part of the tail on the low mass side is removed; now normalisation causes the height of the tail as a proportion of main peak height to increase. Continuing reduction of the source radius further reduces the low mass side of the tail and, at a much smaller radius, the region removed includes the secondary peak. The recent analytical results[11] used a source with radius $0.1 \times r_0$, hence the tail predicted is less than that shown in most of our results.

A real ion source will not have a uniform illumination so the behaviour will not exactly match that of the model used to produce Fig. 6. In most cases the ions will be focused by the ion optic system used to extract them from the source. This will increase the beam intensity close to the axis; consequently, a smaller proportion of the ions will originate at a significant distance from the source and the height of the tail will be reduced. The investigations by W. E. Austin used an ion source with a focusing lens and it is probable that part of the cause of the smaller tail he observed corresponds to this effect. Computations performed with the ion source disc moved so that it was no longer concentric with the QMS axis produced changes in the tail. Interpretation was difficult, and further detailed investigation is necessary, but the results suggest that ions in the tail originated close to the QMS x-axis (as defined in standard references[1]) but at a large distance from the QMS axis.

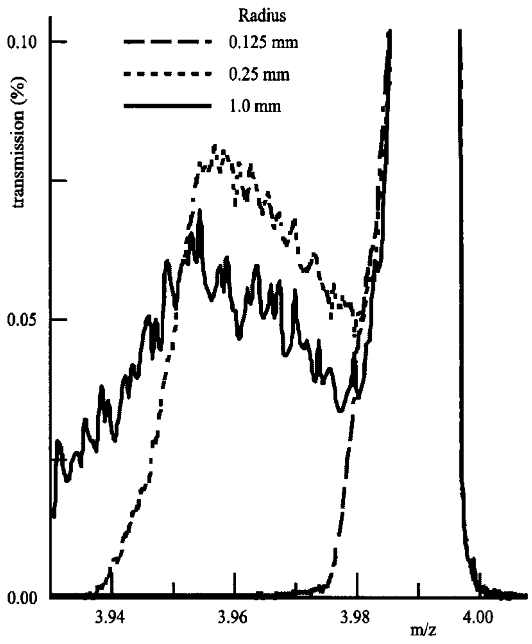

Figure 6. Mass peaks obtained using ion sources with three different radii (main peaks normalised to unity height, $r_0 = 0.276$ mm).

CONCLUSIONS

The tendency of the mass peaks produced by QMS instruments constructed with circular section electrodes to exhibit a tail, in some cases a distinct peak, on the low mass side of the main peak has been shown in experimental observations and by a computer model. This tendency for mass peaks to have a tail on the low mass side is also shown by recent analytical work.[11]

The shape of the tail relative to the main peak is affected by the value of the dimensionless quantity r/r_0; smaller magnitude tails are produced as this quantity decreases from 1.148 down to under 1.125. The tail does not depend on ion mass or energy; however, the number of cycles of the RF field experienced by the ions affects the low mass tail and the main peak differently. After about 80 cycles of the RF field, the main peak is fully formed and changes little if the ions experience more cycles. The low mass region continues to alter as the number of cycles increases, and around 200 cycles are necessary for clear formation of the tail.

The computer model usually predicts a larger tail than that observed. The model shows that the tail depends strongly on the diameter of the ion beam used and the position of the ions relative to the QMS axis. Consequently, the tail will also depend on the spatial distribution of ions within the beam. As a result slight variations in ion source characteristics from one instrument to another will have a significant effect on the low mass side of the spectra produced by QMS instruments.

The model results indicate that to minimise the production of a low mass tail on the mass peaks of a QMS instrument the ion source diameter should be small relative to the QMS radius r_0. Any asymmetric distribution of ions within the source will affect the form of the tail; such effects are complex, but asymmetry causing an excess number of ions to originate close to the QMS x-axis and at a distance from the QMS axis of symmetry (z-axis) will significantly increase the low mass tail.

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