SIMULATION OF A QUADRUPOLE MASS FILTER EMPLOYING A DIGITAL WAVEFORM AND DISCONTINUOUS ION INTRODUCTION TO OBTAIN HIGH RESOLUTION AND TRANSMISSION

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INTRODUCTION

Generally quadrupole mass filters exhibit an inverse relationship between transmission and resolution. Typical commercial quadrupoles, operating in the first stability region, can achieve resolutions of around 5000, although at low transmission (<10%). Operation in higher stability regions can allow higher resolution to be obtained, but results in severe loss of transmission.

Here we present the theoretical basis and computational simulation of a method to obtain simultaneously high resolution and transmission. This comprises driving a quadrupole with a digital EC waveform [1] and pulsing ions into the quadrupole while no drive voltage is applied. The drive voltage is applied at a particular phase once ions have entered the mass filter. Theoretical resolutions (10% valley) over 50,000 can be obtained at greater than 50% transmission.

THEORY

In this poster we compare a quadrupole driven with a conventional harmonic waveform and a digital EC waveform (shown in **figure 1**). The voltages U_1 and U_2 are defined in terms of the Mathieu stability parameters

$$q = \frac{4ze}{m\omega^2 r_0^2} V_{RF} = \frac{2ze}{m\omega^2 r_0^2}\left(U_1 - U_2\right) \qquad (1)$$

$$a = \frac{8ze}{m\omega^2 r_0^2} V_{DC} = \frac{4ze}{m\omega^2 r_0^2}\left(U_1 + U_2\right) \qquad (2)$$

where V_{RF} and V_{DC} are the RF and DC voltages of the harmonic waveform.

Figure 2 shows the stability diagram for the EC waveform used in this work. The insets show example scan lines cutting the upper tips of the r1 and r12 stable regions.

In order to examine the acceptance behaviour of quadrupole mass filters we define the (positional) inverse amplitude phase characteristic (iAPC) as the inverse of the maximum amplitude obtained by a stable ion with an initial positional of 1mm, zero initial velocity. The iAPC is a function of initial RF phase, hence it is effectively a measure of the phase dependent acceptance of the quadrupole with respect to initial position spread. **Figure 3** plots (log scale) the iAPC in the x and y axes for a harmonic quadrupole and an EC quadrupole operating at the r1 tip.

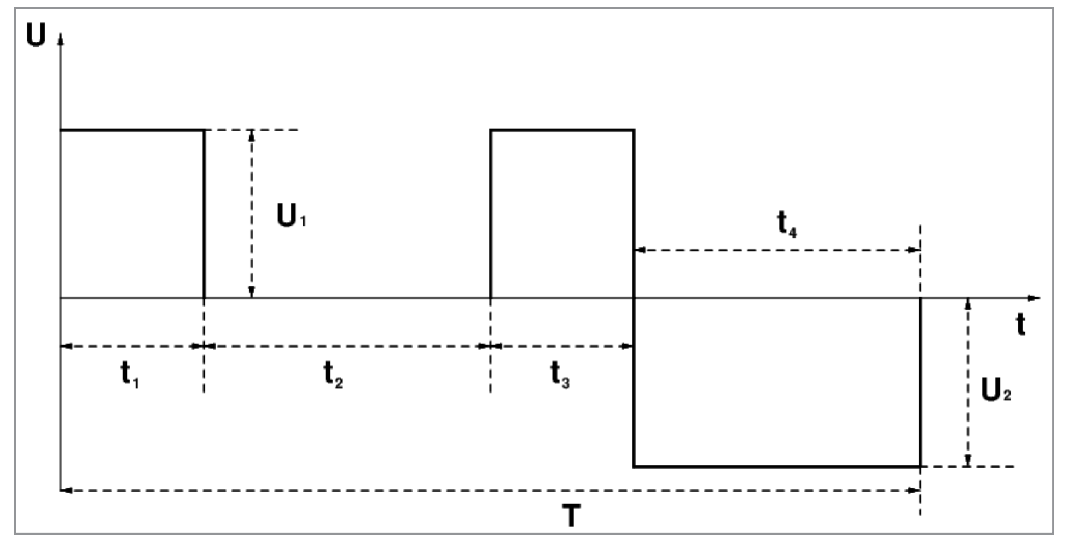

Figure 1. Digital EC waveform over one period T. For the waveform we use here t2=t4=T/3, t1=t3=T/6.

For the harmonic system we plot the iAPC for resolutions of 1k and 10k. We see that the acceptance drops as we increase resolution. At a higher resolution ions that have stable trajectories undergo larger excursions relative to their initial positions, hence more formally stable ions are lost to the rods.

There is a single phase value (π) where we see high acceptance in both x and y axes, this means that if we could arrange all ions to enter the quadrupole on this phase we would have high acceptance with respect to the initial positional spread of the ion beam. This is practically impossible however as the ideal phase range is very narrow, the incoming ion beam has an axial velocity spread, and needs to cross the fringing fields at the entrance of the quadrupole.

For the EC r1 system we plot the iAPC for resolutions of 10k and 50k. While in general we still see lower acceptance at higher resolution there is a large region of initial phase where the acceptance is high in both the x and y axis, and is independent of the resolution. This region corresponds to the zero voltage part of the waveform (time period t_2 in **figure 1**).

The key to obtaining high resolution and transmission is to pulse ions into the quadrupole while zero voltage is applied (i.e. within the high acceptance part of the waveform) and start application of the waveform once ions are fully within the quadrupole (i.e. distant from any fringing fields). In terms of a scan sequence this corresponds to:

1) Trap ions in upstream gas cell while previous scan is occurring.
2) Once the previous scan is over, turn off EC waveform, release the packet of trapped ions into the transfer optics. Reapply trapping potential.
3) Ion packet undergoes phase space manipulation in the transfer optics then passes into the quadrupole.
4) Once the ion packet is sufficiently far inside the quadrupole to be distant from any fringing fields, apply the EC waveform at the correct RF phase.
5) Repeat.

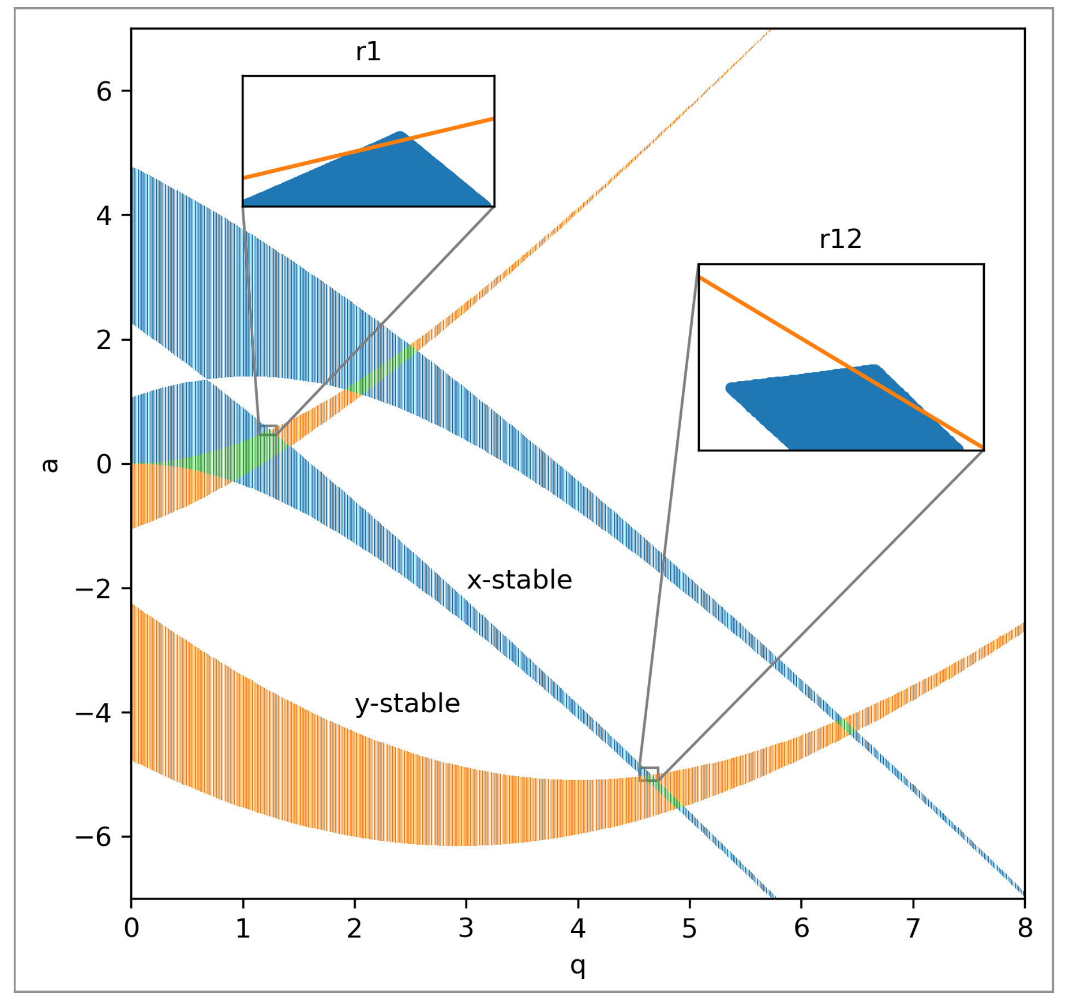

Figure 2. Stability diagram for the EC waveform. Insets show zoomed views of the r1 and r12 stability region tips with example scan lines.

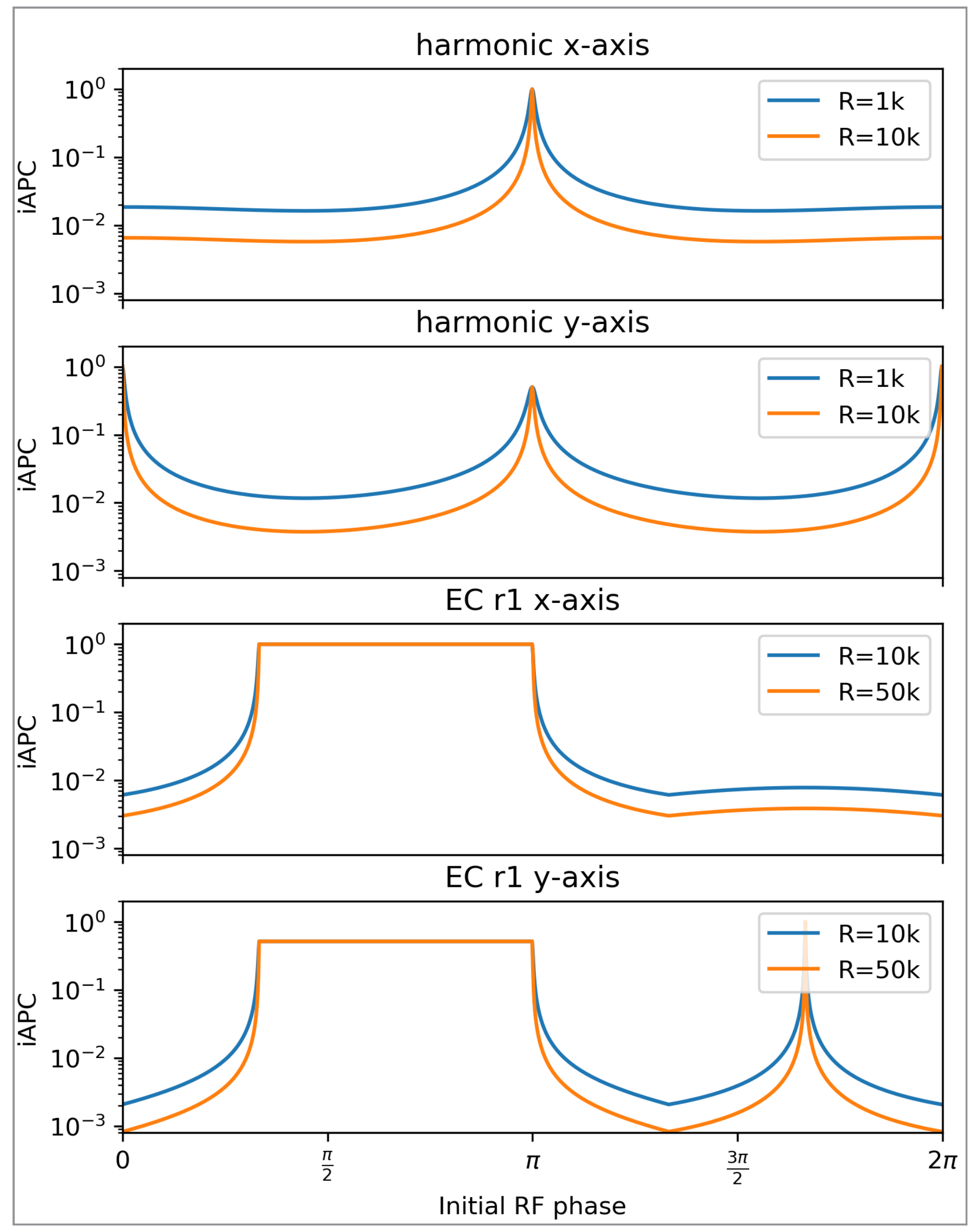

Figure 3. Log iAPC plots for harmonic and EC r1 systems, x and y-axis motion. R=1k/10k for harmonic, R=10k/50k for EC r1.

The iAPCs plotted in **figure 3** consider only acceptance related to initial position. Initial velocity acceptance is not improved by the EC waveform, hence we need to control the initial velocity spread of the ions. Due to the high positional tolerance of the EC system and the conservation of phase space we can use similar transfer optics to those found in oa-TOF instruments to enlarge the positional spread of the ion beam leading to a reduction in the velocity spread. From previous studies expansion of the positional spread of the beam up to a standard deviation of 0.5mm leads to a velocity spread equivalent to a thermal temperature of ~20K.

METHODS

We have implemented the matrix method approach to solving the Mathieu/Hill equation for any given harmonic or digital waveform [2]. This method was used to generate stability diagrams, plots of acceptance vs phase, and to simulate peak shapes for the perfect quadratic field case. For peak shape calculations we run an ensemble of ions at a range of RF/DC values to generate a simulated peak. SIMION 8.1 [3] was used to examine systems with non-perfect quadratic fields and RF waveforms. A grid scale of 64gu/mm was found to be sufficient to reproduce the matrix method results.

Unless otherwise indicated the quadrupole r0 is 4mm, 130mm rod length, 1MHz RF frequency. We use singly charged ions of m/z 556 throughout this poster with an axial energy of 0.2eV. For the 130mm rod length this gives 493 RF cycles for the ions transit time through the quadrupole.

Initial phase space in the normal harmonic system is 0.05mm standard deviation for x/y position, 1000K thermal energy for x/y velocity, uniform distribution of initial RF phase. This distribution is selected to give reasonable agreement with 3D simulations that include a prefilter.

For the EC systems we use 0.5mm standard deviation for x/y position, 20K thermal energy, initial RF phase 2π/3. Note that for the pulsed system we wait for the ions to clear the fringing fields before application of the waveform hence in practice we would lose some effective rod length, the simulations here assume 130mm of rods are present after application of the waveform.

RESULTS

Figure 4 plots 10% valley resolution (R, log scale) vs transmission for harmonic and EC systems. These results are obtained from simulated peaks calculated using the matrix method., i.e. assuming a perfect quadratic field. **Figure 4A** shows the results for the harmonic system, we see the conventional inverse relationship between resolution and transmission, transmission drops from 90% transmission at R=200 to 5% at R=10,000. Although difficult to see in the plot we hit a resolution limit at R~16,000. We also show results for a 0.5MHz system, ions in this case experience half the previous number of RF cycles and show a resolution limit at R~4,000.

This resolution limit is due to the finite transit time of ions through the quadrupole, ions that are formally unstable can still be transmitted if they do not experience a sufficient number of RF cycles. This is known as Von Zahn's rule [4],

$$R_{\max} = \frac{N^2}{c} \qquad (3)$$

where N is the number of RF cycles and c is a constant. For operation at the tip of the first stability diagram values of c in the literature vary from around 12 to 20. We see a limit of R=16,000 which corresponds to c = 15.2, within the range of literature values.

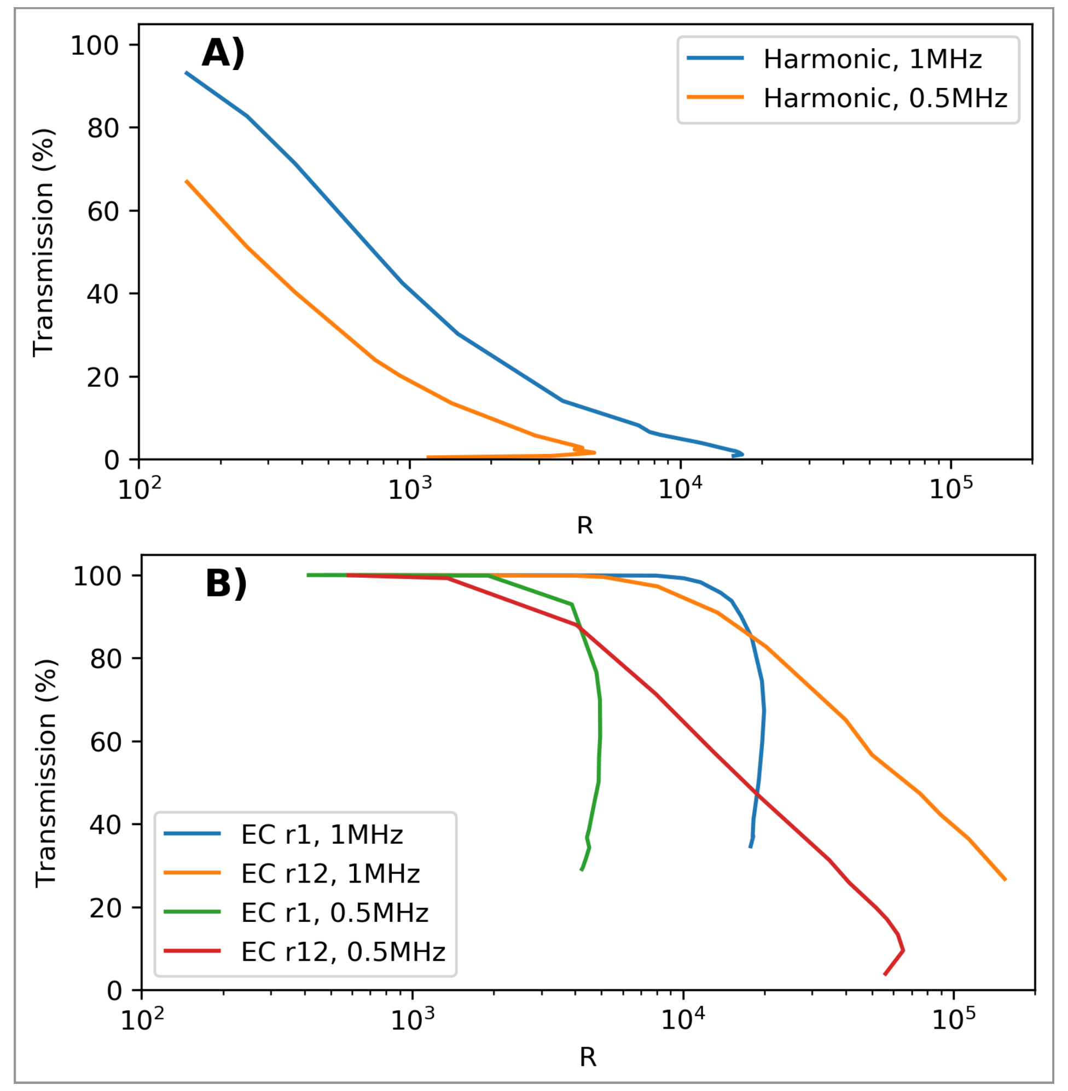

Figure 4. Transmission vs resolution for A) harmonic, B) EC waveform, calculated using the matrix method.

Figure 4B shows the results for the EC waveform. Both stability regions show an initial flat region at 100% transmission up to R~5,000. The r1 region exhibits higher transmission than the r12 after this point until hitting a resolution limit at R~20,000. This gives c = 12.2 for the r1 tip of the EC waveform.

The value of c in equation (3) is significantly lower in higher stability regions leading to higher resolution limits for the same number of RF cycles. For the EC r12 region we can obtain resolutions over 100,000 without reaching a limit. Note that the EC r12 region is less tolerant to initial velocity spread, hence the lower transmission seen relative to the r1 region until we hit the r1 limit.

We also plot results for r1 and r12 regions at 0.5MHz. We see essentially the same behaviour, except now the resolution limits from Von Zahn's rule are a factor of 4 lower, hence we see limits of R~5k for the r1 and R~60k for the r12 region. This allows us to estimate the resolution limit for the r12 region at 1MHz to be ~240,000, giving c ~ 1. With a lower RF frequency we effectively lower the initial velocity tolerance hence we see lower transmission at resolution.

RF drive requirements

In terms of performance it is clearly beneficial to operate at higher RF frequency, however it is practically difficult to drive large voltages at high frequencies. This is especially true for digital systems where the drive of the digital waveform is likely to be a significant limiting factor with current technology. The voltages required for m/z 556 at 1MHz in r1 are +1.3 /-0.8 kV, while in r12 they are +1.9/-6.5 kV. Since voltage scales as f^2 we can see the motivation for operation in the r12 region, at 0.5MHz we only require 0.5/1.6kV while the limit on resolution is still high at 60,000.

Effect of round rods

Figure 5 plots transmission vs resolution for the EC r12 system for SIMION modelled systems compared to the previous matrix method result. For round rods we see severe transmission loss giving a limiting resolution of ~10,000. For hyperbolic rods truncated at 9mm radius we see no significant deviation from the matrix method results. The minor deviation that we observe between SIMION and the matrix method at high resolution is due to the grid scale factor used in SIMION.

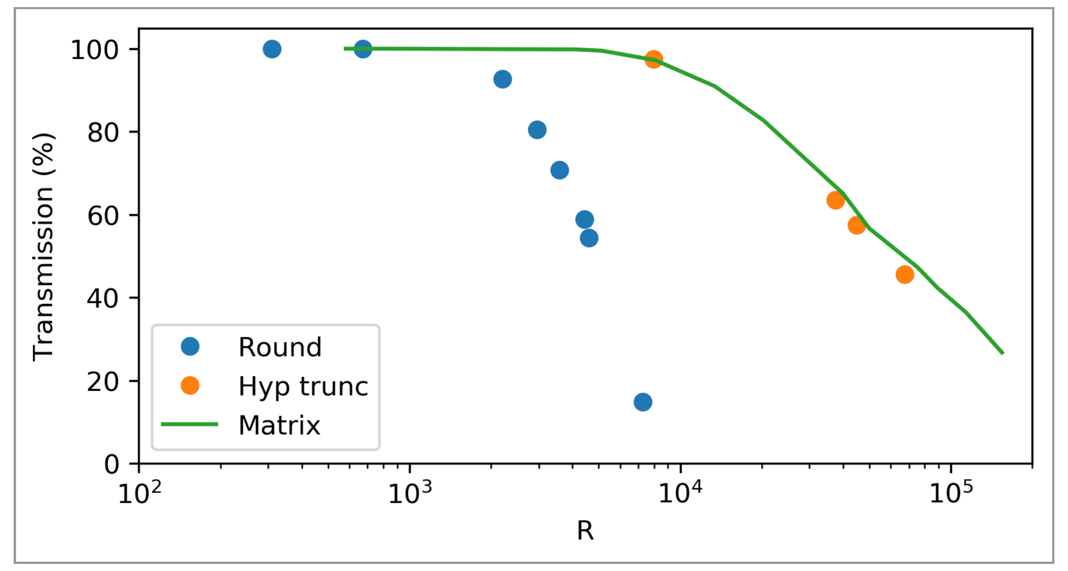

Figure 5. Transmission vs resolution for the EC r12 system using the matrix method, round rods, and truncated hyperbolic rods.

Effect of mechanical misalignment

Figure 6 plots transmission vs resolution for the EC r12 system with truncated hyperbolic rods, where we vary the positional offset of the top rod in the y-axis. As we increase the rod offset the transmission at resolution drops. Current limits to achievable mechanical tolerances are of the order of +/-1 μm, while this may prevent obtaining the extremely high theoretical resolutions (>100,000) we can still obtain, for example, 70% transmission at R=20,000.

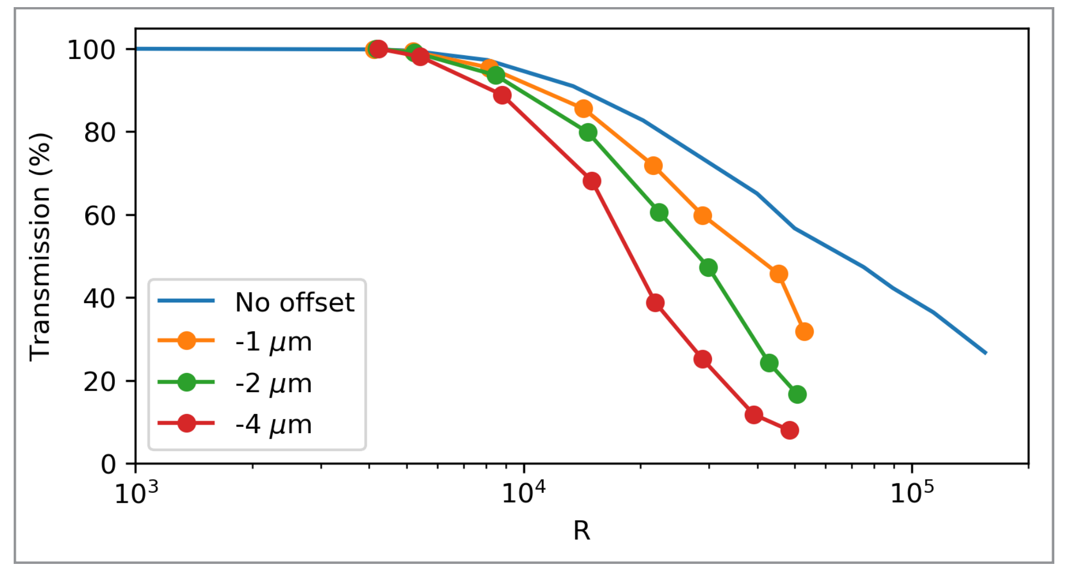

Figure 6. Transmission vs resolution for the EC r12 system for varying y -axis offsets of the top rod.

Effect of timing jitter

We can model the effect of timing jitter by adding a uniform +/- variation on the time of each transition of the digital voltage values. **Figure 7** plots transmission vs resolution for the EC r12 system for a range of jitter values. As we would expect the performance degrades as the jitter increases. For a +/- 1ps jitter we see minimal effect, while for a +/- 20ps jitter we see ~50% transmission at R=10,000.

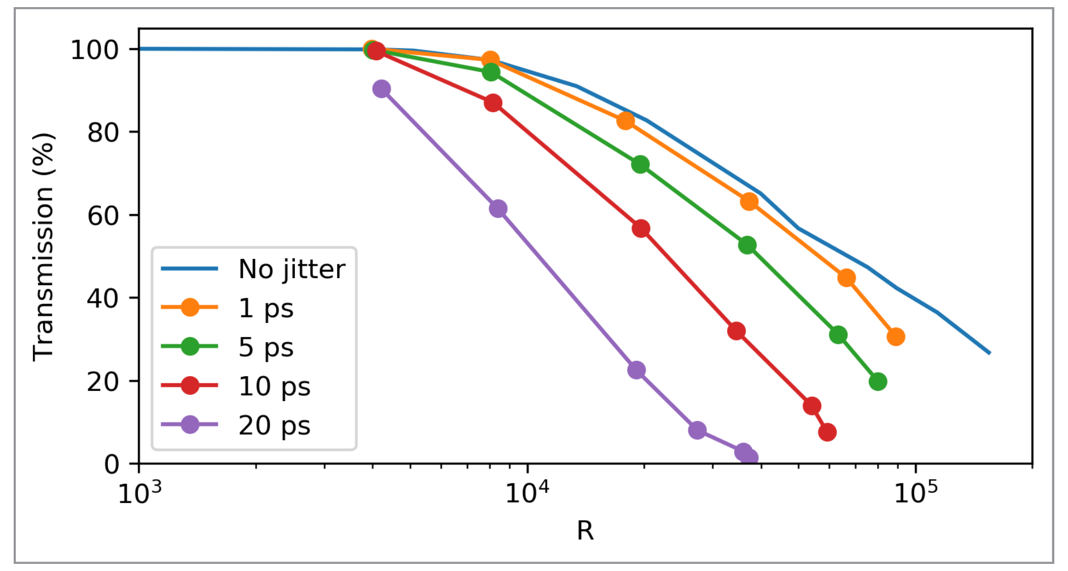

Figure 7. Transmission vs resolution for the EC r12 system for a range of timing jitter values.

CONCLUSION

- **A new method of operating a quadrupole via discontinuous ion introduction and a digital EC waveform.**
- **Theoretical resolutions (10% valley) > 100,000 at significant transmission, and 10,000 at ~100% transmission.**
- **The effect of a range of practical limitations to the theoretical performance have been investigated.**
- **A quadrupole mass filter with a resolution of 10,000 to 20,000 and transmission > 10% does not look unreasonable given current technology.**

References

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