International Journal of Mass Spectrometry 404 (2016) 8–13

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Characterization of quadrupole mass filters operated with frequency-asymmetric and amplitude-asymmetric waveforms

Gregory F. Brabeck[a], Hideya Koizumi[b], Eiko Koizumi[b], Peter T.A. Reilly[a,*]

[a] Washington State University, Department of Chemistry, Pullman, WA 99164, United States
[b] Arkansas State University, Department of Chemistry, State University, AR 72467, United States

ARTICLE INFO

Article history:
Received 1 March 2016
Received in revised form 9 April 2016
Accepted 14 April 2016
Available online 25 April 2016

Keywords:
Digital waveforms
Quadrupole mass filter
Stability diagram
Quadrupolar excitation

ABSTRACT

Since their introduction, digital quadrupole mass spectrometers have described by analogy to traditional sinusoidal devices. However, digital quadrupoles exhibit unique behaviors and simplify many complex ion handling operations due to their uniquely flexible control over the frequency, duty cycle and amplitude of applied potentials. Matrix solutions to the Hill differential equation are used to explore the effects of these additional degrees of freedom on ion stability. Two parameters are explored: varying the frequency ratio of the applied potentials introduces a predictable number of bands of instability to the stability diagram. Varying the amplitude ratio of the applied potentials tunes the width of those unstable bands. Stability diagrams governing a digital mass filter employing asymmetric driving potentials to generate an arbitrary number of pass bands of adjustable width are systematically described.

1. Introduction

Sinusoidal linear quadrupole devices confine ions using one harmonically tuned circuit to generate a pair of driving waveforms 180° out of phase from one another. In contrast, digital linear quadrupoles rely on a pair of high voltage pulse generators to rapidly toggle between two voltages to independently generate the applied potential waveforms for each pair of electrodes. It provides the ability to modulate the duty cycle and frequency of each rod set independently and permits digital quadrupoles to easily perform many operations which would be difficult to achieve in sinusoidally driven ion guides. The ability to switch these parameters at will is crucial for most ion handling operations in the digital ion guide. Demonstrated techniques range from mass filtering [1–3] and controlling axial motion [4] to ultrahigh m/z protein analysis [5] and quadrupole field induced tandem MS [6]. The low mass cut-off (LMCO) of a digital quadrupole is selected by varying the operating frequency rather than the voltage. To date, digital quadrupoles have always been operated with both sets of electrodes switching at the same frequency and voltage, but this is not a requirement. Operating the linear quadrupole with mismatched frequencies and/or potentials generates unique behavior by providing asymmetric quadrupolar excitation to the confined ions while using a fixed duty cycle. This manuscript explores the effects of asymmetric frequency and voltage operation on the stability diagram of the digital linear quadrupole.

2. Methods

2.1. Matrix methods and stability diagrams

The matrix methods developed by Pipes [7], Richards et al. [1], and Sudakov and coworkers [8,9] to provide analytical solutions to the Hill differential equation may be used to calculate ion trajectories [10,11], create phase ellipses to predict ion acceptance [10,12], evaluate pseudopotential well depth [13], and generate stability diagrams [8,14,6] for ions in any periodic quadrupolar field. Describing the functional potential by a finite series of constant-potential segments allows the creation of a series of 2×2 matrices that describe ion motion over the series. If the initial velocity and position of an ion are known then the velocity and position at the end of each constant potential interval may be precisely calculated. These matrices may be multiplied sequentially over any portion of an RF period to define ion motion over that interval. Defining the ion motion over one whole period of the functional potential permits the calculation of the stability parameter, β, at any point in the a, q plane. Evaluating β along the x- and y-axes at many points densely covering a region of q, a space maps the stability diagram. Each diagram below is comprised of 850,000 points.

* Corresponding author.
E-mail address: pete.reilly@wsu.edu (P.T.A. Reilly).

http://dx.doi.org/10.1016/j.ijms.2016.04.002
1387-3806/

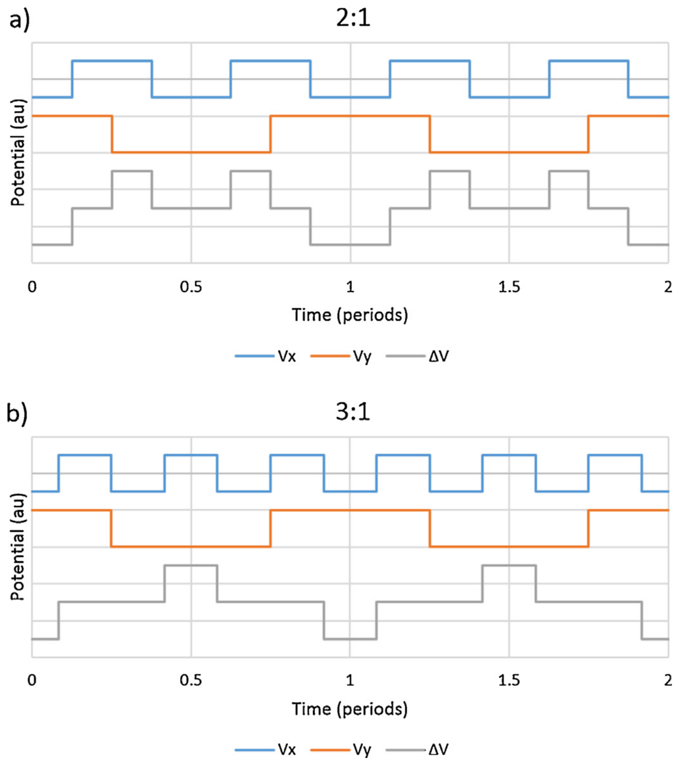

Fig. 1. Two examples of frequency asymmetrical driving waveforms. One RF period is defined as the shortest repeating unit in the functional potential (black). The independently controlled applied potentials (blue and orange) may operate at higher frequencies than the functional frequency. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

This robust technique has been most widely applied to digitally driven systems because only a few calculations are required to precisely define ion motion in these cases. Applications to sinusoidal systems are rarer because the Mathieu equations provide a straightforward way to treat this special case, but matrix methods are equally applicable because they provide a general method to calculate ion motion in any periodic quadrupolar field [6,14].

Matrix methods may also be used to explore the effects of supplemental quadrupolar excitation. Vernier et al. [15] have described the effects of a superimposed low frequency supplemental sinusoidal excitation and examined the role of the relative phase of this excitation on ion stability, but to our knowledge no one has systematically explored the effects of applying asymmetric frequencies and voltages to digitally driven devices.

2.2. Waveform definitions

The period of the quadrupolar field is the shortest repeating unit of the functional potential. In the phase-locked resonantly-tuned sinusoidal devices currently in use, this is simply the period defined by the resonantly tuned circuit. In digital quadrupole devices, each pair of electrodes is controlled independently by a high voltage pulser. This independence permits the potential applied to the two pairs to pass through differing integer numbers of cycles in the same stretch of time. Fig. 1 illustrates two pairs of normalized applied square wave potentials in which the voltage on the x electrodes (blue trace) switches at a different frequency than the voltage on the y electrodes (orange trace). To simplify discussion, all applied potential pairs presented in this work begin 180° out of phase at $t = 0$. The functional potential between the electrodes (black trace, $\Delta V = V_x - V_y$) defines ion motion in the quadrupole device along one of the orthogonal axes. The functional potential along the other orthogonal axis is defined by $-\Delta V$. Note that when V_x and V_y have the same sign, ΔV is less than the peak-to-peak voltage; frequency asymmetric operation introduces field free (or low-field) intervals to the period.

Each frequency pairing in this manuscript is expressed as ν_x:ν_y where ν_x is the number of cycles of the alternating potential applied to the electrodes along the x-axis of a linear quadrupole and ν_y is the number of cycles applied to the electrodes along the y-axis during the period. The simplest non-trivial case is 2:1 wherein the x-axis electrodes experience 2 full cycles while the y-axis electrodes experience only 1 (see Fig. 1a).

If the frequencies of the two applied potentials are expressed as an integer ratio, the resulting quadrupolar field will be periodic. For any rational frequency pairing, the period of the functional potential will be the least common multiple (LCM) of the periods of the applied potentials.

If the ratio describing the applied potentials may be simplified, then multiple periods of the functional potential are captured by the waveform, and dividing the duration of the waveform by the common factor yields the correct period. For example, if Fig. 1b were misinterpreted as a 6:2 frequency ratio, then dividing the period of the waveform by 2 would give the correct ratio, 3:1. If multiple periods of the driving waveform are erroneously treated as a single period, the frequency will be misleadingly low. As we will see shortly, the dependence of the Mathieu parameters on frequency results in distorted stability diagrams in such cases. This frequency dependence also means that matrix calculations using the infinitely long periods resulting from irrational frequency pairings generate nonsensical stability diagrams even while they generate accurate ion trajectories.

Choosing the correct period over which to calculate ion stability is critical for generating physically meaningful results. Fig. 2 illustrates the effect on the calculated stability diagram of treating multiple iterations of the driving waveform as a single period. In the 1:1 diagram, the low mass cut-off (LMCO) of stability zone 1 is located at the accepted value of q ($q = 0.7125$). The apex is also found at the correct location in the q, a plane (0.57, 0.23). The period of this functional potential has been chosen correctly.

The 2:2 waveform includes 2 repeating RF units in the defined period. The result is a stability diagram which has been scaled along both the a and q axes. The origin and extent of this scaling becomes clear when definitions of the dimensionless Mathieu parameters are examined:

$$a = \frac{8zeU}{mr_o^2\Omega^2} \quad (1)$$

$$q = -\frac{4zeV}{mr_o^2\Omega^2} \quad (2)$$

where z is the number of elementary charges on the ion of interest, e is the elementary charge, m is the mass of the ion, r_o is the quadrupole radius, Ω is the angular frequency of the quadrupolar field, V is the zero-to-peak RF voltage, and U is the DC potential between the electrodes. The definitions of U and V are duty-cycle independent [14].

When 2 cycles are included in each period, the frequency used to calculate ion stability, Ω, is reduced by a factor of 2. As a result, the boundary values of a and q are 4 times larger than the accepted values. In the 2:2 case, the low mass cut-off is located at $q = 2.85$. Similarly, the apex (and all other points in the diagram) is scaled by a factor of 4 and is found at (2.3, 0.92). The 3:3 case is scaled up by a factor of 9.

The relative magnitudes of the two applied potentials also have a tremendous effect on the stability diagram. Taken individually, each waveform would generate a unique range of stable masses. It is unsurprising that the behavior resulting from a linear combination