International Journal of Mass Spectrometry 422 (2017) 62–73

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

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

Full Length Article

Nonlinear equations of the ion vibration envelope in quadrupole mass filters with cylindrical rods

Mikhail Sudakov

MS-SIMAX, Bratislavskaya 21 korp. 1, kv. 5, 390035, Ryazan, Russia

ARTICLE INFO

Article history:
Received 29 March 2017
Received in revised form 16 August 2017
Accepted 22 August 2017
Available online 1 September 2017

Dedicated to David Dahl

Keywords:
Quadrupole mass filter
Nonlinear field distortions
Perturbation theory
Envelope equations
Effective potential
Stability islands

ABSTRACT

This paper develops the method of envelope equations to describe the oscillatory motion of ions in quadrupole mass analysers with round rods. Nonlinear equations for the description of the envelope dynamics are obtained taking into account the dodecapole (twelve-pole), the icosapole (twenty-pole) and octopole field distortions. It is shown that the effective potential which determines the ion vibration envelope has a quadratic part, with a magnitude and sign that depend on the location of the ion working point. It also contains a nonlinear part, which does not depend on the ion working point location near the tip of the first stability zone. The motion of ions in quadrupole mass filters with cylindrical rods has a nonlinear character at a theoretical mass resolving power over 1000. In the linear approach, nonlinear effects of the ion motion occur in a narrow zone near the boundaries of the first stability region. This explains low sensitivity of mass analysis within stability islands, which is a direct result of the quadrupole excitations at a frequency different from the main excitation frequency. Thus, the boundaries do not depend on nonlinear field distortions. The results of this theoretical approach are illustrated using the transmission peak shape modelling for mass analysers with different values of the rod radius **r** relative to the inscribed radius $\mathbf{r}_0$.

It is shown, that the 6th and 10th order field distortions never compensate each other. However, the octopole field suppresses them completely in the range $1.115 < r/r_0 < 1.135$, which is considered as an optimum. It is also shown that very substantial improvements in a peak shape can be achieved by adding minor (less than 1%) octopole distortions.

1. Introduction

It would not be a big mistake to say, that al most every modern high-end mass spectrometer includes a linear quadrupole. Quadrupole mass analysers are routinely used as residual gas analysers for vacuum systems [1], as inexpensive mass scanning analysers, for precursor ion mass selection in tandem mass spectrometers [2], as collision cells [3] or ion guides [4], and as linear ion traps with radial [5] or axial [6] ion ejection.

The ideal quadrupole field is created by electrodes with a hyperbolic cross section. However, the manufacturing and assembling of such electrode systems requires anaccuracy in the micron range, which is a difficult and very expensive task. For this reason, many commercial companies use the round rods (cylinders). The field within such mass analysers differs from an ideal quadrupole field and contains nonlinear components. It has been found experimentally, that the optimal geometry of such quadrupole electrode systems has the ratio of the rod radius r to the inscribed radius r_0 lying in the range from 1.115 to 1.130. Originally this fact was obtained experimentally by companies manufacturing quadrupoles. Recently, this has been confirmed theoretically by computer simulations of the transmission peaks for quadrupole mass filters with round rods [7,8].

It has been known from the early history of quadrupole technology development, that the use of cylindrical instead of hyperbolic rods distorts the peak shape. In addition, the peak position shifts when the resolving power is changed. It has been claimed that these distortions are caused by nonlinear resonances of ion vibrations, the effect typical for nonlinear vibrational systems with many degrees of freedom [9]. Dawson and Whetten have attributed this to the sixth order resonance line $\beta_x + 2\beta_y = 1$, that appears close to the Y stability boundary [10]. Such resonances are typical for 3D ion traps operating in the QUISTOR mode, when ions experience over 10^5 RF cycles [11]. For a mass filter, resonances appear [12] at

E-mail address: m.soudakov@yandex.ru

http://dx.doi.org/10.1016/j.ijms.2017.08.017
1387-3806/

$K\beta_x + (N-K)\beta_y = 2$, where K has values of N, $(N-2)$, $(N-4)$, ... and N is the order of the nonlinear resonance [13].

In this paper, to describe ion motion within quadrupole mass filters with cylindrical rods, perturbation theory is applied to derive the equations of ion vibration envelopes. These equations come from nonlinear terms in the original equations of motion, which appear due to deviations of the real field from a pure quadrupole field. The analysis of these equations shows that the above nonlinear resonances do not distort a peak shape because there is insufficient ion residence time inside a quadrupole analyser. All major phenomena, which are typical for quadrupole mass filters with cylindrical rods are explained by the shape of the nonlinear effective potential of the ion vibration envelope. The effective potential has a quadratic part, with magnitudes and signs that depend on the ion working point location. It also contains a nonlinear part, which does not depend on the ion working point location near the tip of the first stability zone. The results of the theoretical approach are illustrated by modelling the transmission peaks for mass analyzers with different values of the ratio of the rod radius to the inscribed radius r/r_0.

We also show here that the motion of ions in quadrupole mass filters with cylindrical rods has a nonlinear character at a theoretical resolving power over 1000. Nonlinear effects of the ion motion occur in a narrow zone near the boundaries of the first stability region. This explains the low sensitivity of mass analysis within stability islands, which is a direct result of quadrupole excitation at a frequency different from the main RF frequency. Thus, the boundaries do not depend on nonlinear field distortions.

It is shown, that the 6th and 10th order field distortions never compensate each other. However, an octopole field suppresses them completely in the range $1.115 < r/r_0 < 1.135$, which is considered optimum. It is also shown that very substantial improvements in a peak shape can be achieved by adding minor (less than 1%) octopole distortions.

2. Field distortions in quadrupole mass filters with cylindrical rods and the equations of ion motion

An ideal quadrupole mass filter consists of four conductive electrodes with hyperbolic cross sections. They are arranged parallel to the common axis Z and are spaced by the distance r_0 from the center (Fig. 1). A radio frequency (RF) voltage $V(t)$ is connected positively to one pair of rods (the X– rods) and negatively to the other pair (the Y– rods), creating a 2D electric field among the rods, with a potential given by:

$$\Phi(x,y,t) = V(t)\cdot\Phi(x,y). \quad (1)$$

For mass analysis, the applied voltage has both DC (U) and radio-frequency (V) components:

$$V(t) = U + V\cdot Cos\left[\Omega t + \alpha\right]. \quad (2)$$

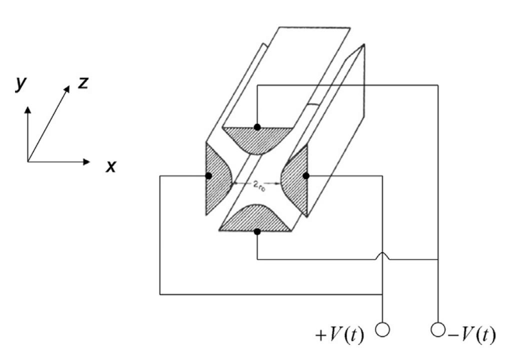

Fig. 1. Electrode system of quadrupole mass filters with hyperbolic rods.

Here Ω– is the angular frequency of the RF power supply and α – is the initial phase.

The function $\Phi(x, y)$ in Eq. (1) describes the potential distribution of the electric field inside a quadrupole analyser. A method of a very accurate computation of this function is described in [14] for quadrupole analysers with cylindrical rods. Nonlinear field distortions are also analysed for such electrode systems. It has been found that the major field distortions in quadrupole analysers with cylindrical rods are the twelve-pole harmonics, which can be characterised by a dimensionless multipole amplitude A_6, and the twenty-pole harmonic with the amplitude A_{10}. Considering these distortions, the potential function for the electric field can be written in the following form:

$$\Phi(x,y) = A_2\frac{x^2-y^2}{r_0^2} + A_6\frac{p_6(x,y)}{r_0^6} + A_{10}\frac{p_{10}(x,y)}{r_0^{10}}, \quad (3)$$

where A_2 is the amplitude of the quadrupole field. In analysers with an ideal field this parameter is equal to one: $A_2 = 1.0$. For analysers with cylindrical rods this parameter differs slightly from one. Here r_0 is the inscribed radius of the quadrupole mass filter ("the field radius"). The field distortions are described by the following functions

$$p_6(x,y) = x^6 - 15x^4y^2 + 15x^2y^4 - y^6, \quad (4.a)$$

$$p_{10}(x,y) = x^{10} - 45x^8y^2 + 210x^6y^4 - 210x^4y^6 + 45x^2y^8 - y^{10}, \quad (4.b)$$

The equations of ion motion in such a 2D field are the following:

$$M\frac{d^2x}{dt^2} + eV(t)\cdot A_2\frac{2x}{r_0^2} = -eV(t)\cdot\left[\frac{A_6}{r_0^6}\cdot\frac{\partial p_6(x,y)}{\partial x} + \frac{A_{10}}{r_0^{10}}\cdot\frac{\partial p_{10}(x,y)}{\partial x}\right], \quad (5.a)$$

$$M\frac{d^2y}{dt^2} - eV(t)\cdot A_2\frac{2y}{r_0^2} = -eV(t)\cdot\left[\frac{A_6}{r_0^6}\cdot\frac{\partial p_6(x,y)}{\partial y} + \frac{A_{10}}{r_0^{10}}\cdot\frac{\partial p_{10}(x,y)}{\partial y}\right]. \quad (5.b)$$

Here M is the ion mass and e is the charge. Ions move with a constant velocity along the Z axis. Let us assume that RF voltage, applied to the electrodes of the analyser is harmonic: $V(t) = U + V\cos(\Omega t + \alpha)$. Now we introduce dimensionless variables with the following definitions

$$a = A_2\frac{8eU}{M\Omega^2 r_0^2},\ q = A_2\frac{4eV}{M\Omega^2 r_0^2}. \quad (6)$$

Instead of time we introduce the dimensionless variable $\xi = (\Omega t + \alpha)/2$ and measure all dimensions in the units of r_0. This means that instead of actual x and y coordinates of an ion we consider the same variables divided by r_0: $x \to x/r_0$ and $y \to y/r_0$. After such a transformation we obtain the equations of ion motion in the following form

$$x'' + (a + 2q\cos\xi)\cdot x = f(x,y,t)\cdot x, \quad (7.a)$$

$$y'' - (a + 2q\cos\xi)\cdot y = g(x,y,t)\cdot y, \quad (7.b)$$

where

$$f(x,y,\tau) = -(a + 2q\cos 2\xi)\cdot[6\alpha_6\cdot(x^4 - 10x^2y^2 + 5y^4) + 10\alpha_{10}\cdot(x^8 - 36x^6y^2 + 126x^4y^4 - 84x^2y^6 + 9y^8)], \quad (8.a)$$

$$g(x,y,\tau) = -(a + 2q\cos 2\xi)\cdot[-6\alpha_6\cdot(y^4 - 10y^2x^2 + 5x^4) - 10\alpha_{10}\cdot(y^8 - 36y^6x^2 + 126y^4x^4 - 84y^2x^6 + 9x^8)]. \quad (8.b)$$

Here τ is a dimensionless time unit measured from the end of each n^{th} RF cycle: $\xi = n\pi + \tau$, where $n = 1, 2,$.... Here we also introduced the relative amplitudes of nonlinear distortions according to the following definitions

$$\alpha_6 = \frac{A_6}{2A_2} \text{ and } \alpha_{10} = \frac{A_{10}}{2A_2} \quad (9)$$