International Journal of Mass Spectrometry 408 (2016) 9–19

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

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

Possibility of operating quadrupole mass filter at high resolution

Mikhail Sudakov[a,*], Eugenij Mamontov[a], Fuxing Xu[b], Chongsheng Xu[b], Chuan-Fan Ding[b,*]

[a] Ryazan State Radio Engineering University, 390035, Gagarina 57, Ryazan, Russia
[b] Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry and Laser Chemistry Institute, Fudan University, 220 Handan Road, Shanghai, China

ARTICLE INFO

Article history:
Received 12 July 2016
Received in revised form 7 September 2016
Accepted 7 September 2016
Available online 9 September 2016

To the memory of Vladimir Vladimirovich TITOV.

Keywords:
Quadrupole mass filter
Stability islands
Residence time
High resolution
Faster mass scan
Quadrupole excitation
One dimensional filtering
Increment of instability
Nonlinear field distortions

ABSTRACT

A new possibility of improving the resolving power of quadrupole mass filters has been studied theoretically in this work. The results show that with the use of two AC excitations, in addition to the main RF supply, it is possible to modify the first stability diagram for mass filtering by creating a narrow and long band of stability along the *X* boundary near the tip of first stability region. These newly developed stability regions (the *X*-band) are similar to higher stability regions, and offer high mass resolution and fast mass separation features. This approach overcomes the many limitations of the normal operation of quadrupole analyzers, while retaining the advantages of using the first stability region. The new operation mode could achieve up to 10,000 mass resolving power with the ion residence time of only 100 RF cycles. In addition, the ion transmission efficiency with the use of the *X*-band is not only compromised, but is greater than in the normal operation mode. Furthermore, the new mode features one-dimensional mass filtering (in the *X* direction only) that is not sensitive to nonlinear field distortions, which are particularly problematic for quadrupole mass filters which built with circular rods. Faster mass separation has been confirmed in simulations and theoretical computations of the exponential increment of the trajectory instability. Due to the location of the *X*-band near the tip of the first stability region, the new operation mode can still have the benefits of traditional techniques (delayed DC ramp) for overcoming the negative effects of fringe fields and improving the ion transmission efficiency. The theoretical simulations show that the method of improving the performance of quadrupole mass filters does not require any modifications of mechanical structures, and only needs different and a little more sophisticated method of electric applications.

1. Introduction

Over half a century has passed since the invention of mass analysis of ions using the quadrupole radio frequency field by W. Paul [1]. Nowadays, the different type of ion traps and quadrupole mass analyzers have been applied in wide fields because of their very strong analytical capabilities and compact sizes. Quadrupole mass filters (QMF or quadrupole analyzers) are routinely used in physics and analytical chemistry as standalone mass spectrometers, a part of tandem mass spectrometry for parent ion selection, ion guides for ion beam transmission, or collisional cells for precursor ion fragmentation. Filtration of ions in a quadrupole mass analyzer system is based on the properties of the Mathieu equation that describes the ion motion in quadrupole fields with a harmonic power supply [2]. Thus, the quadrupole mass filtering technology requires a high precision of machining and assembling of electrodes with micrometer accuracy, and a development of very stable and controllable power supplies for generating high frequency and high voltage signals (RF supply).

Although quadrupole mass filtering technology has been well established and investigated both experimentally and theoretically in the past several decades, a search for new and unusual modes of operation is on going. Quadrupole analyzers with a distorted electrode geometry [3,4] and with periodic quadrupole excitations (additional AC power supply with different frequency on top of main RF) [5,6] have been investigated over many years in D. Douglas' laboratory. In spite of the common knowledge that the efficient ion filtration is only achievable with the use of high quality quadrupole fields [7–10], it was found that quadrupole analyzers with significantly modified electrodes can be successfully used for ion filtration under certain conditions [3]. Moreover, the use of

* Corresponding authors.
E-mail addresses: m.soudakov@gmail.com (M. Sudakov), cfding@fudan.edu.cn (C.-F. Ding).

http://dx.doi.org/10.1016/j.ijms.2016.09.003
1387-3806/

additional periodic excitations can overcome the destructive influence of nonlinear electric field distortions and obtain a comparable resolving power and ion transmission efficiency with commercial devices [6].

This paper reports a new possibility of operating a quadrupole analyzer at high mass resolution. The "high mass resolution" means the filtering of ions with the mass resolving power significantly greater than 5000, which is a practical maximum for quadrupole mass filters when operating in a normal mode. In this paper, we will first discuss the principle and properties of a normal operation mode of quadrupole mass filters that leads to some basic limitations and possible ways of overcoming them. We further study the possibilities for the most appropriate mass filtering by modifying the stability diagram of ion motion. These modifications are possible with the use of special periodic excitations that result in new properties of the ion motion. It will show that the separation of ions under the new mode occurs much faster than in a normal operation mode and it allows a high resolution mass separation in spite of a short residence time of ions inside a quadrupole analyzer. The proposed mode of operation is verified by direct simulations of ion motion in a two-dimensional quadrupole field where the resolving power of a mass separation and ion transmission efficiency are compared with a normal operation mode under similar conditions. The result of the faster ion separation rate is explained by greater increments of trajectory instability from both sides of the stability regions, and the increments are computed theoretically. A new mode of operation is not sensitive to nonlinear distortions of the quadrupole field, which is confirmed by simulations of the mass peak shapes in quadrupole analyzers with cylindrical rods. Finally, the implications of the new operational mode for some modern mass filtering techniques are discussed.

2. The normal mode of quadrupole mass filter operation and its limitations

2.1. A quadrupole mass filter and equations of ion motion

A conventional quadrupole mass filter is composed of four conducting rods with an ideal hyperbolic cross section [1]. They are arranged parallel to the common Z axis and are equally spaced by a distance r_0 from the center. An RF voltage $V(t)$ is connected positively to one pair of the rods (the X rods) and negatively to another pair of the rods (the Y rods), resulting in the quadrupole field among the rods:

$$\Phi(x,y) = V(t)\cdot\frac{x^2-y^2}{r_0^2}. \tag{1}$$

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

$$V(t) = U - V\cdot Cos(\Omega t+\alpha). \tag{2}$$

Here, Ω is the angular frequency of the RF power supply and α is its initial phase. An ion motion in such field is usually expressed in terms of dimensionless variables:

$$\frac{d^2x}{d\xi^2} + (a + 2qCos2\xi)\cdot x = 0, \tag{3.a}$$

$$\frac{d^2y}{d\xi^2} - (a + 2qCos2\xi)\cdot y = 0, \tag{3.b}$$

where

$$\xi = \frac{\Omega t+\alpha}{2},\ \mathrm{a} = \frac{8eU}{M\Omega^2 r_0^2},\ \mathrm{q} = \frac{4eV}{M\Omega^2 r_0^2} \tag{4}$$

M is the ion mass and e is its charge.

2.2. Stability diagram and mass filtering

Both Eqs. (3.a) and (3.b) are linear, second order differential equations with periodic coefficients known in literature as the Mathieu equations [11]. Note that the parameters of Eq. (3.a) are taken for a basis while parameters for the Y motion have an opposite sign. The Mathieu equation appears in physics as a mathematical model for a description of a parametric resonance, but there are some regions of a and q parameters for which the parametric resonance does not occur and which correspond to a stable motion. The graphical description of these regions on a plane of a and q parameters is termed as "a stability diagram". Ions can be transmitted through a quadrupole analyzer if only both X and Y motions are stable simultaneously. The regions where the stability diagrams of the X and Y motions overlap are called the regions of common stability or "stability zones". There is an infinite number of such regions. The first zone of the common stability, called "the first stability region" (see Fig. 1), is usually used for conventional quadrupole mass filtering.

It is evident from Eq. (4) that for ions of different mass-to-charge ratio, a and q parameters appear at the same "operating" line $a = \lambda\cdot q$, where $\lambda = 2U/V$. The a and q parameters are inversely proportional to the ion mass, so heavy ions have parameters ("working point") located closer to the origin of the diagram. By an appropriate selection of the U/V ratio, the operating line can be located so that it crosses the tip of the first stability region, as shown in Fig. 1. The mass filtering method in quadrupole analyzers is evident – only ions that have mass-to-charge ratio within some range $[M_{\min}, M_{\max}]$ will have stable motion inside a quadrupole mass filter. When a beam of ions of different mass-to-charge ratios is injected into a quadrupole analyzer, the heavier ions experience instability in the Y direction and are ejected by the Y rods, while the lighter ions are unstable in the X direction. Only the ions that have working points within a stable zone will be transmitted to the end of the quadrupole analyzer and then detected by an ion detector. The mass selection using a stability triangle at the tip of the first stability region is referred further as "a normal" or "a conventional" mode of the quadrupole analyzer operation.

2.3. The resolving power of a mass selection in a normal mode of operation

The mass resolution is defined by the width of a transmitted mass range $\Delta M = M_{\max} - M_{\min}$ and is usually expressed in Thomson unit which has been introduced by Prof. G.Cooks [12] as an appropriate measure of the mass-to-charge ratio, 1 Thomson equals 1 Da mass unit $1.66053873\cdot10^{-27}$ kg divided by the electron charge $1.602176462\cdot10^{-19}$C. The mass resolving power, R, is a dimensionless measure that is equal to the ratio of the nominal mass, $M_{nom} = (M_{\min} + M_{\max})/2$, and the transmitted mass range, ΔM:

$$R = \frac{M_{nom}}{\Delta M}. \tag{5}$$

In practice, quadrupole analyzers, are operated by scanning RF voltage amplitude, while keeping the U/V ratio fixed (when scanning in a wide mass range, the U/V ratio is adjusted slightly in order to keep a similar resolution at each mass) and recording ion current at a detector. The mass assignment is obtained from the RF voltage, V, using a definition of q parameter from Eq. (4):

$$M_{nom} = \frac{4e}{\Omega^2 r_0^2}\cdot\frac{V}{q_1}. \tag{6}$$

Here, $q_1 = 0.705996$ is the coordinate value of the stability tip. In experiments, the mass resolution, ΔM, is defined for ion species of similar mass as the peak width measured at some level of the peak maximum (usually 10%).