
Mass Analysis in Islands of Stability with Linear Quadrupoles with Added Octopole Fields

Nikolai Konenkov

Department of General Physics, Ryazan State Pedagogical University, Ryazan, Russia

XianZhen Zhao, Zilan Xiao, and D. J. Douglas

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada

Mass analysis with linear quadrupole mass filters is possible by forming “islands” in the stability diagram with auxiliary quadrupole excitation. In this work, computer simulations are used to calculate stability boundaries, island positions, and peak shapes and ion transmission for mass analysis with linear quadrupole mass filters that have added octopole fields of about 2 to 4%. Rod sets with exact geometries that have quadrupole and octopole fields only in the potential, and round rod sets, with multipoles up to $N = 10$ (the twenty pole term) included in the calculations, show the same stability boundaries, island positions, and peak shapes. With the DC voltage applied to the rods so that the Mathieu parameter $a < 0$, conventional mass analysis is possible without the use of an island. With the DC polarity reversed so that $a > 0$, the resolution and transmission are poor preventing conventional mass analysis. In principle, mass analysis in an island is possible with operation at either of two tips. Provided the correct island tip is chosen for mass analysis, peak shapes comparable to those with $a > 0$ and no excitation are possible, both with $a > 0$ and with $a < 0$. In the latter case, the use of an island of stability allows mass analysis when the added octopole otherwise prevents conventional mass analysis. (J Am Soc Mass Spectrom 2007, 18, 826–834) © 2007 American Society for Mass Spectrometry

Linear quadrupole ion traps are finding increasing use in mass spectrometry [1]. Ions can be stored for tandem mass spectrometry [2, 3] or confined and manipulated before injection into other mass analyzers, such as time-of flight [4], Paul trap [5], ion cyclotron resonance [6], or electrostatic (“Orbitrap”) [7] analyzers.

As with three-dimensional Paul traps [8], the addition of field distortions to a linear quadrupole ion trap can improve MS/MS efficiency [9] or give faster ejection of ions at a stability boundary [10]. The field distortions are described mathematically by the addition of higher spatial harmonics or multipole fields to the quadrupole field. Methods to add octopole [9c, 11] or hexapole [12] fields to linear quadrupoles have been described.

In some applications [3], it is desirable that a linear trap used for MS/MS is capable of mass analysis. Various methods of mass analysis with linear quadrupoles have been described. Conventionally, DC and RF potentials can be applied between the rod pairs [13] to

place ions to be mass analyzed at a tip of a stability region to produce a mass filter. The addition of higher multipoles to the field has, in the past, been expected to degrade the performance of a linear quadrupole operated as a mass filter in this way [14]. Nevertheless, it has been found that linear quadrupoles with added octopole [15] and hexapole fields [12a] can in fact be operated as mass filters, provided the DC voltage is applied to the electrodes with the correct magnitude and polarity. Ions can also be mass analyzed in a linear quadrupole by radial ejection through slots in the rods [2]. Alternatively, axial ejection can be used for mass analysis with a linear quadrupole, either with or without trapping of ions. Ions within the quadrupole are excited by dipole or quadrupole excitation, gain sufficient kinetic energy to overcome a potential barrier at the quadrupole exit, and are ejected [3, 16]. Preliminary experiments show that this method can be used for mass analysis with a linear quadrupole that has an added octopole field [17].

For operation as mass filters, linear quadrupoles can also be operated with “islands of stability” formed by parametric excitation of ions produced by excitation with auxiliary quadrupole RF or by amplitude modulation of the RF voltage [19]. In a mass filter with a pure quadrupole field, the potential, $V(x, y, t)$, is

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Address reprint requests to Dr. D. J. Douglas, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, V6T 1Z1, Canada. E-mail: douglas@chem.ubc.ca

$$V(x, y, t) = \left(\frac{x^2 - y^2}{r_0^2}\right)\varphi(t) \quad (1)$$

where x and y are Cartesian coordinates, and r_0 , the field radius, is the distance from the centre to an x or y electrode. With quadrupole excitation, the time-dependent potential applied to the electrodes, $\varphi(t)$, is given by

$$\varphi(t) = U - V_{rf}\cos(\Omega t - \phi_0) - V'\cos\omega_{ex}t \quad (2)$$

where U is the DC potential applied from an electrode to ground, V_{rf} the amplitude of the main RF voltage with angular frequency Ω applied from pole to ground, ϕ_0 is the initial RF phase, and V' is the amplitude of the quadrupole excitation voltage with angular frequency ω_{ex} . With no damping, motion of an ion in the potential of eqs 1 and 2 is determined by

$$\frac{d^2x}{d\xi^2} + (a - 2q\cos[2(\xi - \xi_0)] - 2q'\cos 2v\xi)x = 0 \quad (3)$$

$$\frac{d^2y}{d\xi^2} - (a - 2q\cos[2(\xi - \xi_0)] - 2q'\cos 2v\xi)y = 0 \quad (4)$$

where the dimensionless parameters are defined as:

$$\begin{aligned} \xi &= \frac{\Omega t}{2}; \quad \xi_0 = \frac{\phi_0}{2} \\ a &= \frac{8ezU}{m\Omega^2 r_0^2}; \quad q = \frac{4ezV_{rf}}{m\Omega^2 r_0^2} \\ v &= \frac{\omega_{ex}}{\Omega}; \quad q' = \frac{4ezV'}{m\Omega^2 r_0^2} = q \frac{V'}{V_{rf}} \end{aligned} \quad (5)$$

and m is the ion mass, e is the electron charge, and z is the number of charges on the ion.

The angular frequencies of ion oscillation in a quadrupole field, ω_u , are given by

$$\omega_u = (2n + \beta_u) \frac{\Omega}{2} \quad (6)$$

where u is x or y , β_u is a function of the a and q parameters, and $n = 0, \pm 1, \pm 2, \dots$. With quadrupole excitation, resonances are excited when

$$\omega_{ex} = |l + \beta_u| \frac{\Omega}{K} \quad (7)$$

where $K = 1, 2, 3, \dots$ [20] and $l = 0, \pm 1, \pm 2, \pm 3, \dots$.

If $v = \frac{Q}{P}$ where Q and P are integers, the β values of the quadrupole resonances are determined by

$$\frac{Q}{P} = \frac{|l + \beta_u|}{K} \quad (8)$$

The stability diagram forms $P - 1$ relatively strong resonance lines for the x and y motions [18c]. Near the tip of the stability diagram, where $\beta_x \approx 1$ and $\beta_y \approx 0$, when $v < 1$, the strongest resonances occur for the x motion with $\beta_x = Q/P$ ($l = 0$ and $K = 1$ in eq 8) and for the y motion with $\beta_y = 1 - \frac{Q}{P}$ ($l = -1$ and $K = 1$ in eq

8). The stability diagram forms bands of instability along iso- β lines, with β_u values given by eq 8. Islands of stability are formed between the bands of instability [18, 19]. Ions of a particular mass to charge ratio (m/z) can be mass analyzed by adjusting the applied RF and DC voltages to place ions at the tip of an island. Ions of other mass to charge ratios lie outside the stability island and are not transmitted. A mass scan is performed by changing the RF to DC voltages with a constant ratio U/V_{rf} to bring ions of different m/z ratios to the tip of the stability island. Provided the excitation conditions (v, q') are correctly chosen, a scan line can be produced that passes through the island with the greatest a, q parameters without intersecting other islands of stability. As with a conventional mass filter, the resolution can be adjusted by changing the ratio U/V_{rf} . The resolution can be adjusted by changing the ratio U/V_{rf} during a scan to produce the desired peak width (e.g., unit resolution) over the mass range. However the lowest resolution possible will be determined by the width of the stability island ($q/\Delta q \approx 90$ with $v = 9/10$ and $q' = 0.020$).

In principle, islands of stability provide an alternate method for mass analysis with linear quadrupoles with added multipoles. The use of an island of stability may allow operation of the rod set as a mass filter under conditions where the added multipoles otherwise compromise mass analysis. The potential in a quadrupole with an added octopole field and no other multipoles, is given by

$$V(x, y, t) = \left[A_2 \left(\frac{x^2 - y^2}{r_0^2} \right) + A_4 \left(\frac{x^4 - 6x^2y^2 + y^4}{r_0^4} \right) \right] \phi(t) \quad (9)$$

where A_2 and A_4 are the dimensionless amplitudes of the quadrupole and octopole terms respectively. With quadrupole excitation, $\varphi(t)$ is given by eq 2. (For the potential of eq 9, the distance from the center to an x electrode is approximately $\frac{r_0}{\sqrt{A_2}} \left(1 - \frac{A_4}{2A_2^2} \right)$ and to a y electrode approximately $\frac{r_0}{\sqrt{A_2}} \left(1 + \frac{A_4}{2A_2^2} \right)$). With an added octopole field, and with $U > 0$ ($a > 0$ in eq 5), the boundaries of the stability diagram without excitation are like those of a pure quadrupole field, and are well defined, so that conventional mass analysis is possible. Conversely, when $U < 0$ ($a < 0$) the stability boundaries

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