International Journal of Mass Spectrometry 287 (2009) 114–118

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

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

The concept of electrostatic non-orbital harmonic ion trapping

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ARTICLE INFO

Article history:
Received 3 November 2008
Received in revised form 22 January 2009
Accepted 23 January 2009
Available online 3 February 2009

Keywords:
Electrostatic trap
Harmonic motion
Ion motion
Cassinian equation

ABSTRACT

A new, more general type of electrostatic ion trap mass analyzer is described. The potential distribution of the electrical field in this trap can be expressed as a combination of a quadrupolar and logarithmic-Cassinian potential. As the field can be described, in part, by the Cassinian equation the trap is called a Cassinian trap. One mode of the Cassinian trap allows for a one-dimensional trapping motion. This is the first time a one-dimensional trapping motion has been theorized in combination with a harmonic analysis motion in an electrostatic trap. The one-dimensional trapping motion allows ions to be introduced and trapped readily in the Cassinian trap. Theoretically, a mass range of a factor of 50 can be accommodated.

1. Introduction

Electrostatic orbital ion trapping was first shown by Kingdon [1]. The ideal Kingdon trap consists of a wire along the center-axis of a long tube. If an electric potential is applied between the wire and the tube an electric field attracts ions to the wire. If the ions have the proper kinetic energy perpendicular to the attracting direction they will orbit around the wire thus the ions will be trapped. If the tube is infinitely long, the electric potential, $\Psi(r)$, between the wire and the tube can be expressed by the one-dimensional equation:

$$\Psi(r) = \frac{\ln(r/ri)}{R_{\ln}} \cdot U_{\ln} + U_{off} \quad (1)$$

where $R_{\ln} = \ln(ro/ri)$, the wire diameter is $2ri$ and the inner diameter of the tube is $2ro$. U_{off} corresponds to the voltage applied to the wire and $U_{\ln} + U_{off}$ the voltage applied to the tube. Makarov [2] showed in his paper in 2000 that ions can be trapped in orbits around the inner electrode while simultaneously conducting an axial harmonic oscillation. This trap is commonly known as the Orbitrap. The electric field in an Orbitrap can be expressed as a combination of a quadrupolar and logarithmic potential and can be written as a two-dimensional equation:

$$\Psi(r,z) = \frac{\ln(r/ri)}{R_{\ln}} \cdot U_{\ln} + \frac{2 \cdot z^2 - r^2 - c^2}{R_{quad}} \cdot U_{quad} + U_{off} \quad (2)$$

where $R_{\ln} = \ln(ro/ri)$, $R_{quad} = ro^2 - ri^2$ and $c = ri$. The potential in the Orbitrap will be U_{off} (the voltage of the inner electrode) at $r = ri$ (the radius of the inner electrode at $z = 0$). The potential of the outer electrode $U_{\ln} + U_{off} - U_{quad}$ is reached at $r = ro$ (the radius of the outer electrode at $z = 0$). The mass analysis of this device is derived from the harmonic oscillation of ions along the z-axis [3,4]. The frequency of an ion's oscillation depends on the ion's m/z.

However, there are alternative concepts for constructing electrostatic traps that have harmonic ion oscillations along the z-axis. The potential in one such trap can be described as:

$$\Psi(x,y,z) = \frac{\ln(((x^2+y^2)^2 - 2 \cdot b^2 \cdot (x^2 - y^2) + b^4)/ai^4)}{A_{\ln}} \cdot U_{\ln} + \frac{2 \cdot z^2 - (2-B) \cdot x^2 - B \cdot y^2 - c^2}{A_{quad}} \cdot U_{quad} + U_{off} \quad (3)$$

where $A_{\ln} = \ln(ao^4/ai^4)$, $A_{quad} = 2\,(ao^2 - ai^2)$ and $c^2 = 2ai^2$, and B is a constant.

The numerator of the quotient inside the logarithm corresponds to the well known Cassinian equation [5]:

$$(x^2+y^2)^2 - 2 \cdot b^2 \cdot (x^2 - y^2) + b^4 = a^4 \quad (4)$$

Hence this trap should be named Cassinian trap, where the equation for the Orbitrap is just a subset wherein $r^2 = x^2 + y^2$, $b = 0$, $ai = ri$, and $ro = ao$.

This leads to the quite obvious description of a combination of a general logarithmic potential with a quadrupole potential:

$$\Psi(x,y,z) = A_1 \cdot \ln(f(x,y)) + A_2 \cdot (2 \cdot z^2 - (2-B) \cdot x^2 - B \cdot y^2) \quad (5)$$

The quadrupole potential alone satisfies already the Laplace equation $\Delta\Psi(x,y,z) = 0$, that applies also to the logarithmic

Abbreviations: LCP, logarithmic-Cassinian potential; 1D, one-dimensional.

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doi:10.1016/j.ijms.2009.01.014

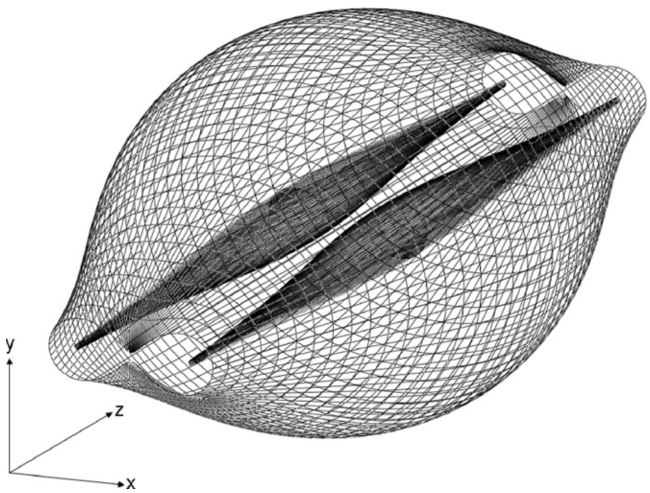

Fig. 1. A 3D plot of a classical Cassinian trap. The grid represents the outer electrodes or receiving plates and the smooth mesh the inner electrodes.

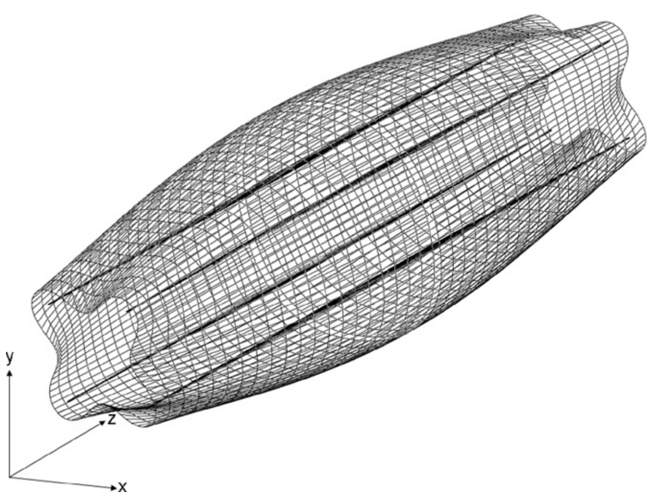

Fig. 2. A 3D plot of a second order Cassinian trap.

potential, which gives a general definition of $f(x,y)$:

$$f(x,y) = \frac{(d/dx(f(x,y)))^2 + (d/dy(f(x,y)))^2}{d^2/dx^2(f(x,y)) + d^2/dy^2(f(x,y))} \tag{6}$$

The function $f(x,y) = x^2 + y^2$ as well as $f(x,y) = (x^2 + y^2)^2 - 2b^2(x^2 - y^2) + b^4$ satisfy this requirement and there are probably more functions.

However, this brings us back to the Cassinian trap. The shape of the outer and inner electrode which corresponds to an equipotential surface can be derived when Eq. (3) is solved for z. z is then a function in x and y. If $\Psi(x,y,z)$ is replaced by the voltage of the outer electrode, z corresponds to z-values for the outer electrode and if $\Psi(x,y,z)$ is replaced by the voltage of the inner electrode, z corresponds to z-values for the inner electrodes. Fig. 1 shows a typical Cassinian trap with the outer electrode as a grid and the inner electrodes as a smooth mesh.

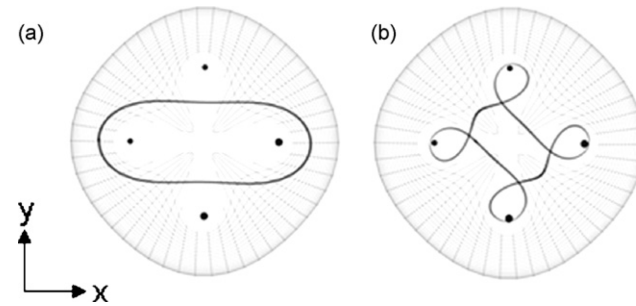

Fig. 4. Additional trapping motions, e.g., in a second order Cassinian trap. (a) Cassinian curve and (b) cloverleaf.

The potential distribution of the field can be expressed as a combination of a quadrupolar and logarithmic-Cassinian potential. The logarithmic-Cassinian potential (LCP) can be turned around the z-axis and so different LCPs can be combined to give Cassinian traps of higher order. To address this, in Eq. (3) x and y are replaced by:

$$g_x(x, y, x_{off_n}, y_{off_n}, \alpha_n) = (x + x_{off_n}) \cdot \cos(\alpha_n) + (y + y_{off_n}) \cdot \sin(\alpha_n) \tag{7.1}$$

$$g_y(x, y, x_{off_n}, y_{off_n}, \alpha_n) = (y + y_{off_n}) \cdot \cos(\alpha_n) - (x + x_{off_n}) \cdot \sin(\alpha_n) \tag{7.2}$$

When different LCPs, with different b-, x_{off}-, y_{off}- and α-values are combined Eq. (3) converts to:

$$\Psi(x,y,z) = \sum_n \left[\frac{\ln(((g_x^2 + g_y^2)^2 - 2 \cdot b_n^2 \cdot (g_x^2 - g_y^2) + b_n^4)/ai_n^4)}{A_{\ln_n}} \cdot U_{\ln_n} \right] + \frac{2 \cdot z^2 - (2 - B) \cdot x^2 - B \cdot y^2 - c^2}{A_{quad}} \cdot U_{quad} + U_{off} \tag{8}$$

E.g., a trap with four inner electrodes (see Fig. 2) which corresponds to an order of $n = 2$.

In the following, the motion along the z-axis will be referred to as the analytical motion. The motion in the x–y plane will be referred to as the trapping motion. The motion along the z-axis is always harmonic. While the trapping motions in the Kingdon trap or Orbitrap are always orbital can the trapping motions in the Cassinian trap may be orbital or non-orbital.

An orbital trapping motion around the inner electrodes of a Cassinian trap is possible (see Fig. 3a). Where the lemniscate like (see Fig. 3b), nephroidic (see Fig. 3c) and especially the one-dimensional (1D) motion (see Fig. 3d) are non-orbital. Higher order traps according to Eq. (8) can exhibit even more trapping motions (see Fig. 4). This is the first time non-orbital harmonic ion trapping in an electrostatic ion trap has been theorized.

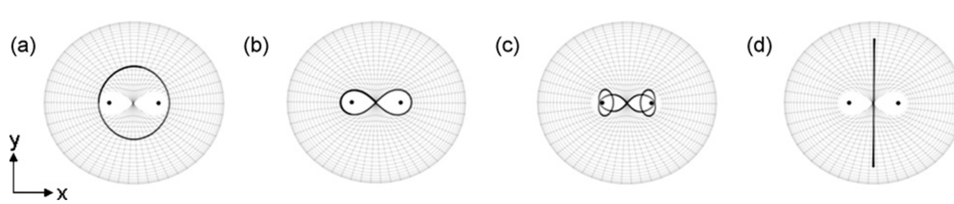

Fig. 3. Trapping motions in a classical Cassinian trap. (a) Orbital, (b) nephroidic, (c) lemniscate and (d) 1D.