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The concept of electrostatic non-orbital harmonic ion trapping

Claus Köster*

Bruker-Daltonik GmbH, EpT, Fahrenheitstr. 4, 28359 Bremen, Germany

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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.

* Tel.: +49 421 2205 167; fax: +49 421 2205 390.
E-mail address: ck@bdal.de.

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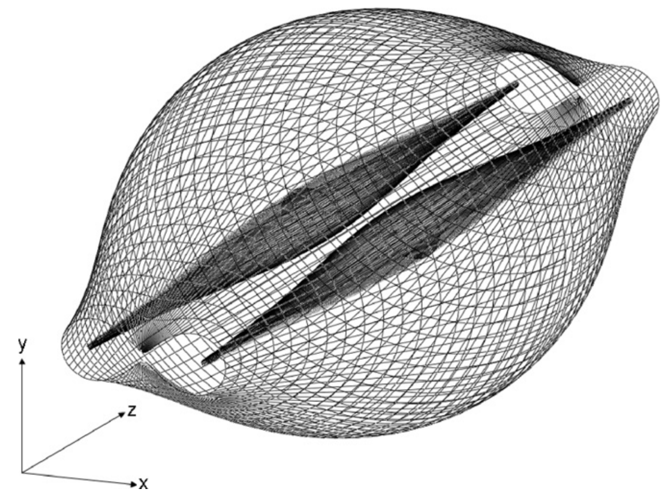

Fig. 1. A 3D plot of a classical Cassinian trap. The grid represents the outer electrodes or receiving plates and the smooth mesh the inner electrodes.

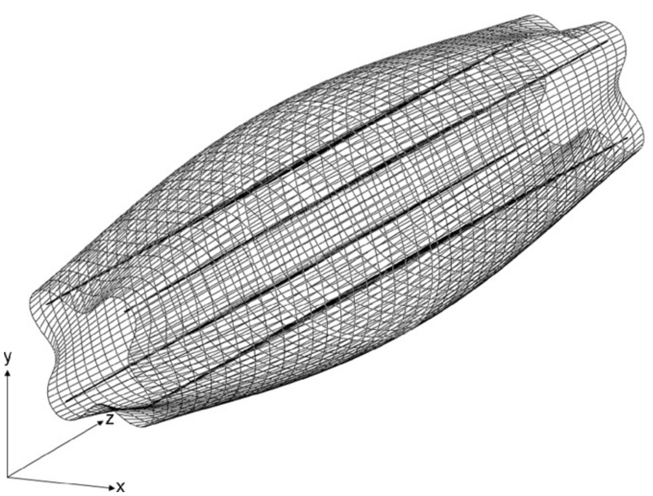

Fig. 2. A 3D plot of a second order Cassinian trap.

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.

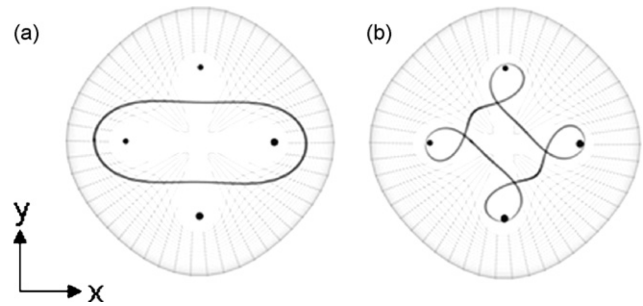

Fig. 4. Additional trapping motions, e.g., in a second order Cassinian trap. (a) Cassinian curve and (b) cloverleaf.

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.

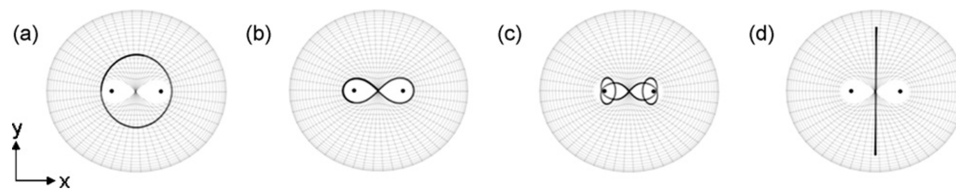

Fig. 3. Trapping motions in a classical Cassinian trap. (a) Orbital, (b) nephroidic, (c) lemniscate and (d) 1D.

Table 1
Cassinian trap parameters used to plot the outer- and inner-electrode surface and ion-trajectories. For Figs. 2 and 4 a second LCP was superimposed to the LCP used for Fig. 3 or 5.

	x_{off} (mm)	y_{off} (mm)	α (°)	ai (mm)	ao (mm)	b (mm)	U_{ln} (V)	B	U_{quad} (V)	$U_{\text{outer-electrode}}$ (V)	$U_{\text{inner-electrode}}$ (V)	U_{off} (V)
Fig. 1	0	0	0	6.5	19	7	900	1	100	1000	0	0
Figs. 3 and 5	0	0	0	6.5	19	7	900	1	100	1000	−800	0
Figs. 2 and 4	0	0	90	6.5	19	7	900					

Table 2
Ions' starting conditions for trajectory calculations.

	Fig. 3a	Fig. 3b	Fig. 3c	Fig. 3d	Fig. 4a	Fig. 4b	Fig. 5
Motion	Orbital	Lemniscate	Nephroidic	1D	Cassinian	Coverleaf	2D
x_0 (mm	10	0	0	0	10	3	3
y_0 (mm)	0	0	0	18	0	−3	18
z_0 (mm)	0	0	0	0	0	0	0
$\text{Angle}_{xy\text{-plane}}$ (°)	90	44	47	0	90	45	0
$\text{Angle}_{yz\text{-plane}}$ (°)	0	0	0	0	0	0	0
E_{kin} (eV)	705	293	100	0	318	95	0

Table 1 summarizes the trap parameters, which served as a basis to describe the electric potential for positive ion trajectory calculations and to plot the shape of the outer and inner electrode for Figs. 1–4.

In Table 2 are shown the ion starting conditions leading to trajectories presented in Figs. 3–5.

The stability of the trajectory of trapped ions varies widely according to the type of trapping motion. For example, the lemniscate like (Fig. 3b) and cloverleaf like motions (Fig. 4b) are highly unstable. Slight changes in the ions' starting conditions lead relatively quickly to collisions with the inner electrodes. In contrast, the orbital (Fig. 3a), nephroidic (Fig. 3c), Cassinian curve (Fig. 4a) and especially the 1D trapping motion (Fig. 3d) are very stable.

2. Theory

The 1D trapping motion is an especially useful trapping motion, because ions with almost no initial kinetic energy can be trapped inside the Cassinian trap. Thus, the remainder of this article will focus on this 1D trapping motion.

2.1. Ion motion

Ions created at an appropriate position within the trap (e.g., by laser ionization of gas phase aromatic hydrocarbons) will be immediately trapped and begin their harmonic motion along the z-axis. Exemplary ion trajectories in a Cassinian trap should be considered. These can be derived by applying the Lagrange-formalism. The force in the direction d, $F_d = m\, a_d$, where m is the mass and a the acceleration towards d is equal to $F_d = -q\, E_d$, where q is the charge and E_d the electric field towards d. The derivative of $\Psi(x,y,z)$ in all three spatial directions yields the electrical field:

$$m \cdot \frac{d^2}{dt^2}x = -q \cdot \left[\frac{4 \cdot (x^2+y^2) - 4 \cdot b^2}{(x^2+y^2)^2 - 2 \cdot b^2 \cdot (x^2-y^2) + b^4} \cdot \frac{U_{\text{ln}}}{A_{\text{ln}}} - 2 \cdot (2-B) \cdot \frac{U_{quad}}{A_{quad}}\right] \cdot x \tag{9.1}$$

$$m \cdot \frac{d^2}{dt^2}y = -q \cdot \left[\frac{4 \cdot (x^2+y^2) + 4 \cdot b^2}{(x^2+y^2)^2 - 2 \cdot b^2 \cdot (x^2-y^2) + b^4} \cdot \frac{U_{\text{ln}}}{A_{\text{ln}}} - 2 \cdot B \cdot \frac{U_{quad}}{A_{quad}}\right] \cdot y \tag{9.2}$$

$$m \cdot \frac{d^2}{dt^2}z = -q \cdot 4 \cdot \frac{U_{quad}}{A_{quad}} \cdot z \tag{9.3}$$

Eq. (9.3) describes a harmonic oscillator. The complete solution of the differential equation is:

$$z(t) = z_0 \cdot \cos(2 \cdot \pi \cdot fz \cdot t) + \sqrt{\frac{m}{2 \cdot q} \cdot vz_0^2 \cdot \frac{A_{quad}}{2 \cdot U_{quad}}} \cdot \sin(2 \cdot \pi \cdot fz \cdot t) \tag{10}$$

where z_0 is the starting position and vz_0 is the starting velocity along the z-axis. The frequency of the ion motion on the z-axis is given by:

$$fz = \frac{1}{2 \cdot \pi} \cdot \sqrt{4 \cdot \frac{q}{m} \cdot \frac{U_{quad}}{A_{quad}}} \tag{11}$$

Eqs. (9.1) and (9.2) are highly nonlinear and difficult to analyze. At least Eq. (9.2) can be analytically solved for $x = 0$:

$$m \cdot \frac{d^2}{dt^2}y = -q \cdot \left[\frac{4}{y^2+b^2} \cdot \frac{U_{\text{ln}}}{A_{\text{ln}}} - 2 \cdot B \cdot \frac{U_{quad}}{A_{quad}}\right] \cdot y \tag{12}$$

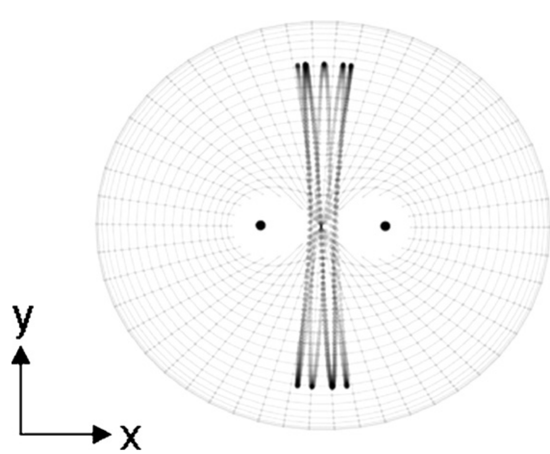

Fig. 5. Trapping motion in a classical Cassinian trap with a distinct starting amplitude in x and y.

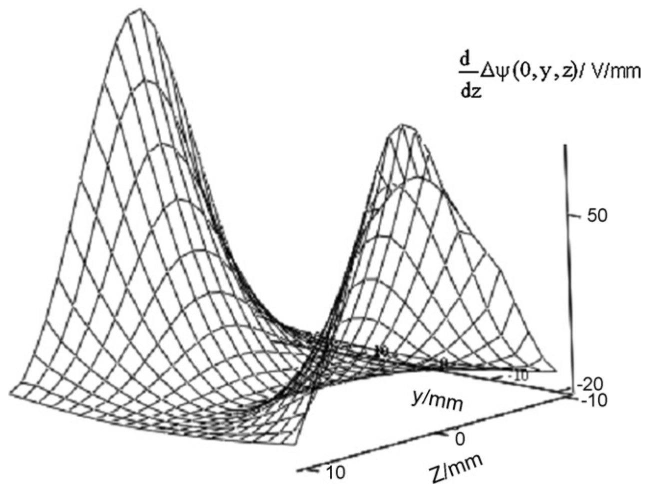

Fig. 6. An example of $d\Delta\Psi(x,y,z)/dz$ at $x=0$ from a SIMION calculation.

Substitution and separation of the variables results in:

$$t(y)=\int_{y_0}^{y}\frac{1}{\sqrt{(q/m)\cdot(4\cdot\ln((y_0^2+b^2)/(y^2+b^2))\cdot(U_{\ln}/A_{\ln})+2\cdot B\cdot(U_{quad}/A_{quad})\cdot(y^2-y_0^2))+\upsilon y_0{}^2}}\cdot dy \tag{13}$$

which is dependent on the starting conditions in y. The motion in y can be approximated as a combination of cosine functions:

$$y(t)=y_{\max}\cdot\frac{\sum_{i=0}^{\infty}ky_i\cdot\cos(ky_i\cdot 2\cdot\pi\cdot fy\cdot(t-ty_{\max}))}{\sum_{i=0}^{\infty}ky_i} \tag{14}$$

where $fy=2/(t(y_{\max})-t(-y_{\max}))$, and the frequency in y, is dependent in the initial values y_0 and υy_0. The maximum amplitude in y, $y_{\max}$, can iteratively be calculated by solving:

$$y_{\max}=\sqrt{\frac{A_{quad}}{B\cdot U_{quad}}\cdot\left(2\cdot\frac{U_{\ln}}{A_{\ln}}\cdot\ln\left(\frac{y_{\max}^2+b^2}{y_0^2+b^2}\right)-\frac{m\cdot\upsilon y_0^2}{2\cdot q}\right)+y_0^2} \tag{15}$$

The motion in x for stable conditions looks like an amplitude modulated carrier frequency. The modulation frequency is fy and the carrier frequency fx:

$$x(t)=\frac{1}{2}\cdot\frac{y_{\max}^2+y(t)^2}{y_{\max}^2}\cdot x_0\cdot\frac{\sum_{i=0}^{\infty}kx_i\cdot\cos(kx_i\cdot 2\cdot\pi\cdot fx\cdot t)}{\sum_{i=0}^{\infty}kx_i} \tag{16}$$

The kx_i respectively the ky_i values have to be adjusted to fit the assumed motion in $x(t)$ and $y(t)$ with the simulation. A stable trapping motion with a distinct starting amplitude in x is shown in Fig. 5.

The matter of ion stability is discussed below in Section 3.

2.2. Ion detection

In an experimental setup, the outer electrode of the Cassinian trap will be split at $z=0$. Ions can be detected by measuring the differentially amplified image current induced on the split outer electrodes. According to Greens's reciprocity theorem [6] and in assuming the absence of any space charge effects and any residue gas, the current induced on an electrode is equal to:

$$I(t)=-\frac{q_{ion}}{\Delta U}\cdot\sum_{ion}\left(\frac{d}{dx}\Delta\Psi(x_{ion},y_{ion},z_{ion})\cdot\frac{d}{dt}x_{ion}+\frac{d}{dy}\Delta\Psi(x_{ion},y_{ion},z_{ion})\cdot\frac{d}{dt}y_{ion}+\frac{d}{dz}\Delta\Psi(x_{ion},y_{ion},z_{ion})\cdot\frac{d}{dt}z_{ion}\right) \tag{17}$$

where q_{ion} corresponds to the charge per ion and ΔU the voltage applied to the electrode which would generate a potential change at x, y and z in the absence of any ions. Each ion induces a change of the potential $\Delta\Psi(x_{ion},y_{ion},z_{ion})$ on the trap electrodes. The sum of the deviations in all three spatial dimensions multiplied by the ion velocity in x, y and z, and averaged over all ions gives the image current. The motion in x and y are not harmonic, so the ions will go out of phase much faster than in the harmonic motion in z. This means that a short time after ion motion is initiated, Eq. (17) can be simplified to:

$$I(t)=-\frac{q}{\Delta U}\cdot N_{ions}\cdot\frac{d}{dz}\Delta\Psi(x,y,z)\cdot\frac{d}{dt}z \tag{18}$$

where N_{ions} is the total number of ions.

SIMION calculations (see Fig. 6.) show that $d\Delta\Psi(x,y,z)/dz$ can be approximated:

$$\frac{d}{dz}\Delta\Psi(x,y,z)=\left(\frac{x^2+y^2}{C^2}\right)^3\cdot\exp\left(-D\cdot\frac{z^2}{x^2+y^2}\right) \tag{19}$$

where C and D are constants. In our special case we consider no space charge effects, just the 1D trapping motion with amplitudes in x close to 0 and a motion in y described by Eq. (14). Averaged in time, an ion stays in x and y close to their reversal points, because the velocity there is near 0. So x and y can be replaced by the average values $\bar{x}=0.64\cdot x_0$ and $\bar{y}=0.64\cdot y_0$.

Thus the expected signal for one type of ion is not just a sine wave but the product of a sine wave with a function which is dependent on the ion location.

$$I(t)=\frac{q}{\Delta U}\cdot N_{ions}\cdot\left(\frac{x_0^2+y_0^2}{C^2}\right)^3\cdot\exp\left(-D\cdot\frac{(z_0\cdot\cos(2\cdot\pi\cdot fz\cdot t))^2}{x_0^2+y_0^2}\right)\cdot 2\cdot\pi\cdot fz\cdot z_0\cdot\sin(2\cdot\pi\cdot fz\cdot t) \tag{20}$$

D is a factor dependent on the trap geometry and the precision of the traps' construction.

2.3. Ion injection

As an example of an ion optically ideal case, ions of a gaseous aromatic compound can be created in a Cassinian trap via a UV-laser beam. When the ions are formed they are immediately trapped. The laser beam can be focused at a point with $z=0$ (*equatorial*) or at a point with $|z|>0$ (*non-equatorial*) (e.g., $x=0$ and $|y|>2\cdot b$). In the equatorial case the laser-beam duration can be very long to accumulate ions. The ions can be formed at $x\sim 0$ and $|y|>2\cdot b$ so they are trapped via a 1D trapping motion. Before signal acquisition the ions have to be excited into motion along the z-axis by applying a short voltage pulse to one of the outer electrodes. In the non-equatorial case the laser-beam has to be switched off shortly before half the period of the oscillation of the smallest m/z ratio to be detected, because the ions begin their z-axis harmonic motion immediately when they are created.

Ions created outside the trap can be trapped by continuously increasing the absolute voltage of the inner electrodes while loading. The potential difference between the inner and outer electrode has to be increased by U_{kin}, the kinetic energy of the ion entering the trap, within duration proportional to the oscillation period, Tz.

$$\frac{d}{dt}U_{el} = \frac{U_{kin}}{k \cdot Tz} \tag{21}$$

Tz can be exchanged by $1/fz$ and within Eq. (11) the mass can be exchanged by $m = 2qU_{kin}(L/t)^2$, where L is the distance the ions travel from the ion source to the trap, and t is the ion's flight time between the source and the trap. Integrating Eq. (21) with the above substitution results in:

$$U_{el}(t) = \left(\sqrt{U_{el0}} + \frac{L}{k \cdot \pi} \cdot \sqrt{\frac{U_{kin}}{2 \cdot A_{quad}}} \cdot \ln\left(\frac{t}{t_0}\right)\right)^2 \tag{21}$$

where t_0 is the flight time of the smallest ion to be trapped and U_{el0} the potential difference between the inner and outer electrode at the entrance of this ion. In general a Cassinian trap can hold ions for U_{el} smaller than 1.25 U_{el0}. This results in a mass range ratio m/m_0:

$$\frac{m}{m_0} = \exp\left(\frac{2 \cdot \pi \cdot k}{L} \cdot (\sqrt{1.25} - 1) \cdot \sqrt{2 \cdot A_{quad} \cdot \frac{U_{el}}{U_{kin}}}\right) \tag{22}$$

For example, assuming $A_{quad} = 6.375 \times 10^{-4}\,\mathrm{m}^2$, $k = 2$, $L = 1$ cm, $U_{kin} = 10$ V and $U_{el0} = 1000$ V is $m/m_0 \approx 50$. So an ion with 50 amu and an ion with 2500 amu can be trapped simultaneously.

3. Discussion

Because the given differential equations are difficult to analyze it is also difficult to come up with general stability criteria. However SIMION calculations show that a combination of parameter b, ai, ao, B and the ratio of $U_{\ln}/U_{quad}$ can be found to create stable trapping conditions. It is quite clear that $ao > b > ai$. For best performance as a mass analyzer, the analytical frequency, fz, should be as high as practically possible. From the above discussion, fz is inversely related to $ao^2 - ai^2$ and is proportional to $\sqrt{U_{quad}}$. However, for stability reasons $U_{\ln}/U_{quad}$ should be approximately 10 or higher. A stable 1D trapping motion in x and y is given for starting coordinates $y > 2b$. Larger starting values in y allows for stable trajectories having a greater deviation in x, vx or vy. Naturally space charge effects can have a significant influence on the ion trajectories and therefore on the measured signal, however, these effects have been left for future studies. Furthermore is it possible to analyze fragment ions produced by metastable decay of parent ions, because the decay is more likely in the area of high probability density. So a high percentage (>60%) of the first daughter ion generation can be trapped and analyzed when injected equatorial and excited in the z-direction.

4. Conclusion

A new, more general type of electrostatic ion trap mass analyzer is described. The potential distribution of the electric 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 1D trapping motion. This is the first time a 1D trapping motion has been theorized in combination with a harmonic analysis motion in an electrostatic trap. The 1D 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.

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