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Impulsional mode operation for a Paul ion trap

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Abstract

The aim of this article is to provide some theoretical basis concerning the impulsional mode of a Paul ion trap using a periodic impulsional voltage of the form $V_0 \cos(\Omega t)/(1 - k\cos(2\Omega t))$ with $k = 0.99$. The performance characteristics of this impulsional mode is illustrated, and compared to the classical sinusoidal mode $k = 0$. Numerical computations allowed the determination of the fractional resolution $m/\Delta m$ of the confined ions, in the first stability regions of both excitation voltage modes. An excellence resolution performance of the impulsional mode can be expected in the lower mass range of 1–2 u, by introducing the same uncertainties values for both operation modes in, machinery accuracy r_0, stability of rf frequency Ω, the rf voltage amplitude $V_{0\rightarrow p}$ and the accuracy of the modulation index parameter k.

Keywords: Confinement; Ions; Paul ion trap; Impulsional mode; Fractional resolution

1. Introduction

The confinement of ions in a narrow stability region of a Paul ion trap with a periodic impulsional voltage of the form $V_0 \cos(\Omega t)/(1 - k\cos(2\Omega t))$ with $k = 0.8$ was constructed and tested, and ultimately compared its performance with the classical sinusoidal form $k = 0$ [1–3]. Since that time, the technological progress in the performance of machining a hyperboloidal geometry ion trap with a good mechanical accuracy, order of $\Delta r_0 = 10^{-3}$ mm and also, good stability in the form and amplitude amplification of the large set of harmonics frequency of rf driving voltage, order of magnitude $\Delta V/V = 10^{-6}$ at a frequency $\Omega \approx 2\pi \times 10^6$ rad/s, provide a wide range of opportunities in the designs and constructions of the diverse type of the Paul ion traps.

Having successfully generated an impulsional voltage signal with the modulating "index" parameter $k = 0.8$ [2], it is thought to increase the modulation index up to $k = 0.99$, in order tightening more and more the stability diagram for the ion movements. This reduction of the stability diagram will in terms bring two criteria; the first of all in some experiments, it is necessary to keep the energy of the injected ion into the trap center constant and ultimately well defined. This can be achieved only if the ion sees no electric field on his path, that is to says, injected in an area of large zero-voltage temporal zone of the impulsional voltage. The possible applications of interest will be in the performance of hybrid tandem mass spectrometry.

Secondly, reduction in the stability region will produce a larger separation between the ion masses in the U-V stability diagrams. Thus, as will be seen, this form of impulsional voltage is perhaps a possible challenge to the existing classical sinusoidal voltage for the Paul ion trap for light isotopic separations in the range of 1–4 u.

The subject of the present study, which is a part of a joint project of constructing a Paul ion trap of multi disciplinary functions, is directed to a general survey of the ion confinement in the first and second regions of the Hill and the Mathieu stability diagrams for the values of $k = 0.99$ and $k = 0$, respectively. The mechanical properties of both voltage signals for the same operating points β_z in their corresponding stability diagrams are compared. The fractional resolutions, using the same uncertainties values as in Refs. [4,7] for the both voltage signals, are compared and presented.

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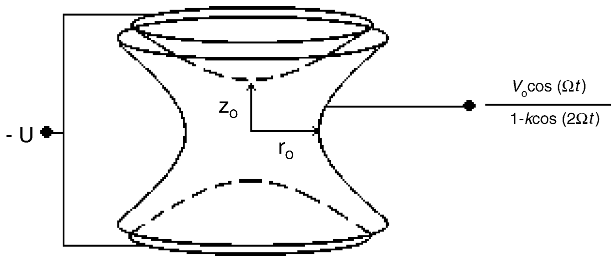

Fig. 1. The electronics configuration.

2. Theory

2.1. Ion movement

The confinement of ions in a narrow region of first Hill stability diagram using an impulsional voltage of the form $V_0\cos(\Omega t)/(1-k\cos(2\,\Omega t))$ with $k=0.8$ and it comparison with the classical Mathieu ion trap with $k=0$, has been presented elsewhere [1–3]. Here, a brief discussion of the method will be presented.

For the electronics configuration shown in Fig. 1, the basic equation of the ion motion is described by Hill's differential equation and is given by

$$\frac{\partial^2 u(\xi)}{\partial \xi^2}+\left[a_u-2I_u\frac{\cos(2\xi)}{1-k\,\cos(4\xi)}\right]u(\xi)=0 \tag{1}$$

where $\xi=\Omega t/2$, $0<k<1$ is the modulation "index" parameter and the trapping parameters a_z and I_z are given as

$$a_z=\frac{-4eU}{mz_0^2\Omega^2}=-2a_r,\qquad I_z=\frac{2eV_k(1-k)}{mz_0^2\Omega^2}=-2I_r \tag{2}$$

If $k=0$, the basic classical ion movement is given by the Mathieu differential equation as follows:

$$\frac{\mathrm{d}^2u(\xi)}{\mathrm{d}\xi^2}+(a_u-2q_u\,\cos 2\xi)u=0,\quad \xi=\frac{\Omega t}{2} \tag{3}$$

Here the trapping parameters a_z and q_z are as follows:

$$a_z=\frac{-4eU}{mz_0^2\Omega^2}=-2a_r,$$
$$q_z=\frac{2eV}{mz_0^2\Omega^2}=-2q_r,\quad V_{k=0}=V \tag{4}$$

where m is the ion mass, e the electric charge, $\Omega/2\pi$ the rf drive frequency, $V_0=(1-k)\ V_k$, V_k is the maximum value of $V_{0\rightarrow\mathrm{p}}$, z_0 is one-half the shortest separation of the end cap electrodes, $r_0^2=2z_0^2$ is the square of ring electrode radius.

The numerical solution of the Hill's differential equation by matrix techniques was extensively discussed in Refs. [5,6]. Here, we give only a brief discussion of the method. For an ion motion stability in the fundamental period $\xi=\pi$, and in the absence of space charge effects, ion–ion or ion–neutral collision, the solution of Eq. (1) can be written as

$$\begin{bmatrix}u(\xi_\circ+\pi)\\ \dot{u}(\xi_\circ+\pi)\end{bmatrix}=M\begin{bmatrix}u(\xi_\circ)\\ \dot{u}(\xi_\circ)\end{bmatrix} \tag{5}$$

where M is a 2×2 matrix and the stability diagram is found by comparing the trace values of the state transition matrix M with the number two, i.e. $|m_{11}+m_{22}|\leq 2$ for a given values of the stability parameters a_z and I_z and

$$m_{11}=\cos(\beta_z\pi)+\alpha_z(\xi_\circ+\pi)\,\sin(\beta_z\pi),$$
$$m_{22}=\cos(\beta_z\pi)-\alpha_z(\xi_\circ+\pi)\,\sin(\beta_z\pi) \tag{6}$$

where $\beta_z=2\omega_z/\Omega$, ω_z is the ion secular frequency.

2.2. Expression of fractional resolution

The resolution of a Paul ion trap mass spectrometer in general, is a function of the mechanical accuracy of the machined hyperboloid ring of the Paul ion trap Δr_0, and the stability performances of the electronics device such as, variations in voltage amplitude ΔV, the rf frequency $\Delta\Omega$ [7] and in our case a new parameter Δk which tell us, how accurate is the form of the voltage signal. The factor Δk is introduced purely from practical point of view, as it plays an important role in building the stability diagram for the purpose of the mass resolution. The ideal case for higher resolution value is when $\Delta k=0$.

To derive a useful theoretical formula for the fractional resolution, one has to recall the stability parameter of the impulsional excitation for the Paul ion trap

$$I_z=\frac{2eV_k(1-k)}{mz_0^2\Omega^2} \tag{7}$$

By taking the partial derivatives with respect to the variables of the stability parameters I_z, then the expression of the resolution Δm of the Paul ion traps will be written as

$$\Delta m=\left(\frac{8eV_k(1-k)}{r_0^3\Omega^2I_z}\right)|\Delta r_0|+\left(\frac{4e(1-k)}{r_0^2\Omega^2I_z}\right)|\Delta V| + \left(\frac{8eV_k(1-k)}{r_0^2\Omega^3I_z}\right)|\Delta\Omega|+\left(\frac{4eV_k}{r_0^2\Omega^2I_z}\right)|\Delta k| \tag{8}$$

By rearranging Eq. (8), the final expression for the fractional resolution is given by

$$\frac{m}{\Delta m}=\left\{\left|\frac{\Delta V}{V}\right|+2\left|\frac{\Delta\Omega}{\Omega}\right|+2\left|\frac{\Delta r_0}{r_0}\right|+\left|\frac{\Delta k}{1-k}\right|\right\}^{-1} \tag{9}$$

This expression indicate that the major contributor to fractional resolution improvement or degradation, at least from theoretical point of view, is the high sensitivities dependency of the resolution to the voltage form and stability and the geometrical machining tolerance.

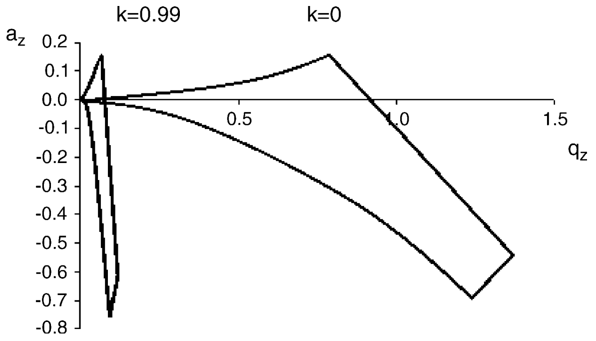

Fig. 2. The first stability regions for $k = 0$ and 0.99.

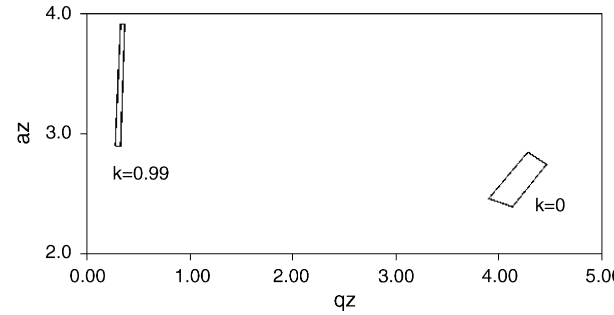

Fig. 3. The second stability regions for $k = 0$ and 0.99.

3. Results

3.1. Stability diagrams

A finite difference method is used to determine the matrix elements of M. The calculations is demonstrate the operation of the Paul ion trap for the confinement of ion in the first and second stability diagrams with the following conditions; $r_0 = 10$ mm, $\Omega = 2.1\pi \times 10^6$ rad/s and Δt the step size is equal to 10^{-11} s. The results of the calculations for the first stability regions in the (a_z, q_z) plane for $k = 0$ and 0.99 are illustrated in Fig. 2. As can be seen, the apex of the stability parameters a_z stayed constant, but the higher limit of I_z decreases substantially when $k = 0.99$. The same parameters as in the first stability diagrams are taken to determine the second stability regions and the result is displayed in Fig. 3. The narrow second stability regions have distance themselves away from the axes a_z and I_z and their values change appreciably, when compared to the first stability regions. This behavior impose certain constraints to the ion movement; the reduction in the stability diagram is provided by increasing the amplitude of the harmonic elements in the voltage signal and if there will be an instability in these elements, the result will be some shifts in the ion secular frequency. So, as long as the amplitude of the harmonic elements stays constant the problem is not significant.

A part from higher harmonics in the impulsional voltage signals, the differ values of a_z for both voltages is also significant. However, it is not clear to what extent one can confine the ions in the narrow second stability regions of a Paul ion trap, as the stability of the rf driving voltage form and the amplitude may cause some problems.

3.2. Ion trajectories

The mechanical properties of the confined ions were examined through the ion displacements and displayed both in real time and in the phase space. For this aim, the same operating points in the first and second stability diagrams are chosen. The results of our computational investigations are shown in Figs. 4 and 5, respectively. The operating points used to find these figures are as follows; $\beta_z = 0.5$ for the first stability diagrams and $a_z = 0$, $q_z = 0.640$ for $k = 0$, and $a_z = 0$, $I_z = 0.045$ for $k = 0.99$, and in the second stability diagram $\beta_z = 1.57$ and, $a_z = 2.630$, $q_z = 3.849$ for $k = 0$ and $a_z = 3.386$, $I_z = 0.284$ for $k = 0.99$.

It is important to know that the β_z point are the equivalent points; two operating points located in their corresponding stability diagram having the same β_z. The ion trajectories in the

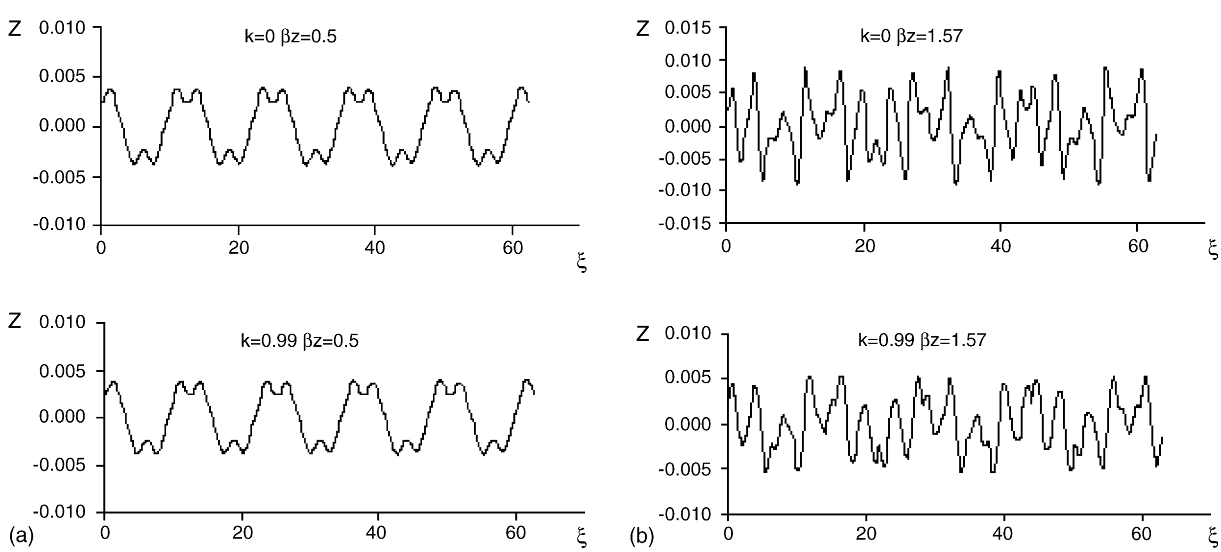

Fig. 4. Ion trajectories in real time for (a) $\beta_z = 0.5$ and (b) $\beta_z = 1.57$.

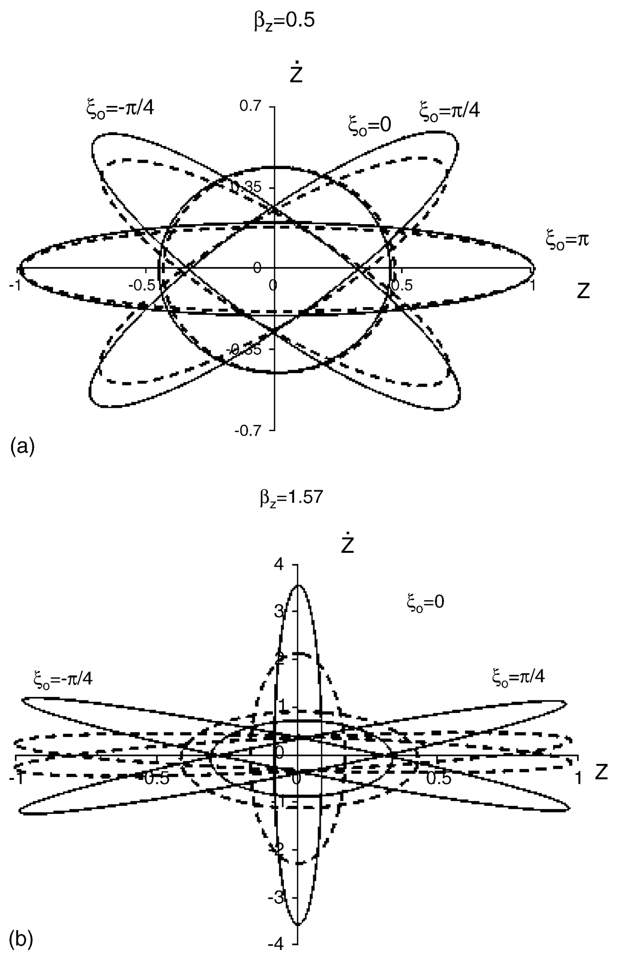

Fig. 5. Ion trajectories in the phase space for (a) $\beta_z = 0.5$ and (b) $\beta_z = 1.57$.

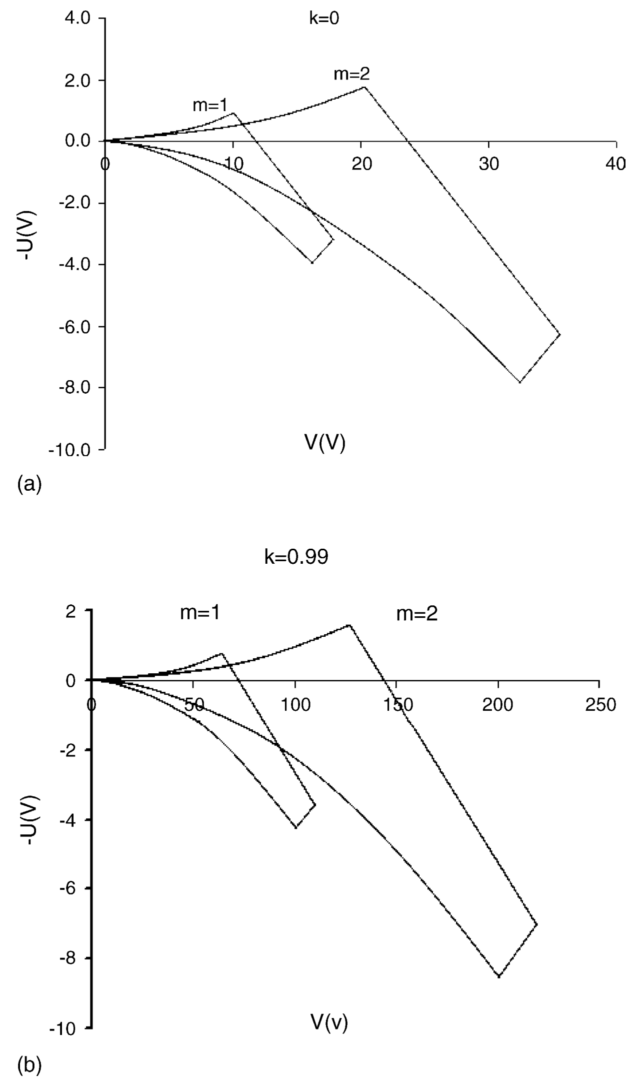

Fig. 6. The stability diagram in (U, V) plane for $m = 1$–2 u: (a) $k = 0$, (b) $k = 0.99$.

first stability regions behave fairly the same, but different in the second stability regions for the following reasons.

The ion motion in both first and second stability diagrams has two frequency components; the ion secular frequency with a characteristic frequency of $\omega = \beta\Omega/2$ and the rf microfrequency in the superposition of several subcomponents with fundamental frequency Ω and its multiplications $n\Omega$ ($n = 2,3,\ldots$), and amplitude modulated with frequency of ω. The number of appreciably contributing subcomponents and their weights strongly depend on the value of the parameters "a_z" and "I_z" [8]. However, the amplitude of the micro frequency in the second region is comparable with that of the secular frequency. But in the first region the former if less or even much less that the latter.

3.3. Fractional resolutions

The operating of a classical Paul ion trap mass spectrometer with fractional mass resolution $m/\Delta m = 1565$ in the lower mass range of 1–4 u has been demonstrated in Ref. [4]. Here, we are intend to examine the actual resolution of a classical Paul ion trap in the lower mass range in the impulsional mode of operation with $k = 0.99$. We confine our work to the first stability regions of both signals.

By the use of the stability parameters a_z and I_z it is possible to establish the first stability diagrams in the (U, V) plane. Fig. 6 shows the stability diagrams in (U, V) plane for the mass range of $m = 1$–2 u (hydrogen and hydrogen like isotopes) and the following parameters: $r_0 = 10$ mm, $\Omega = 2.1\pi \times 10^6$ rad/s with $k = 0$ and 0.99.

From Fig. 6, it is seen that, the stability regions for equal masses are much larger for the new mode of Paul ion trap operation. The difference in the apex values of two masses in terms of the horizontal axes, are equal to about 70 V for $k = 0.99$ and about 10 V for $k = 0$. This means that, there will be approximately seven times more confining voltage needed for the impulsional voltage than the sinusoidal one for the same ion mass-to-charge ratio.

For the simplicity, a formula such as $V_k = n_k V_{k=0}$ can be written for V_k were the coefficient n_k should be found by solving the equation of Hill for different k and the stability regions in the ($-U$, V_k) plan. Table 1 presents the value of the coefficients n_k for the different values of k.

Table 1
relation of n_k and k; $V_k = n_k V_{k=0}$

k	n_k
0	1
0.2	1.1
0.4	1.3
0.6	1.5
0.65	1.6
0.7	1.7
0.8	2
0.9	2.6
0.95	3.5
0.97	4.3
0.99	7

Now, if for example the trap function in rf only mode, an instability about ΔV in the sinusoidal voltage will cause more number of ion masses rich the instability conditions, when compared to the impulsional case. Thus theoretically, the overall result will be a better resolution in mass for the impulsional mode, if all the parameters affecting the resolution are kept constant.

With the aim of implementing the impulsional voltage for the Paul ion trap fractional resolution in the lower mass range (up to Helium like masses) in mind, a similar data as in Ref. [4] for $k = 0$ is used. Fig. 7 presents the evolution of the fractional resolution as the modulation "index" parameter k increases. The following data is used from Ref. [4] to build Fig. 7: the inner radius of the hyperboloid ring $r_0 = 10$ mm, the geometrical uncertainties $\Delta r_0 = 3 \times 10^{-3}$ mm with $\Delta r_0/r_0 = 3 \times 10^{-4}$, the rf frequency uncertainties $\Delta\Omega/\Omega = 10^{-7}$ and the voltage uncertainties $\Delta V = 10^{-4}$ for $k = 0$. For lower mass rang $m = 1$–2 u, the

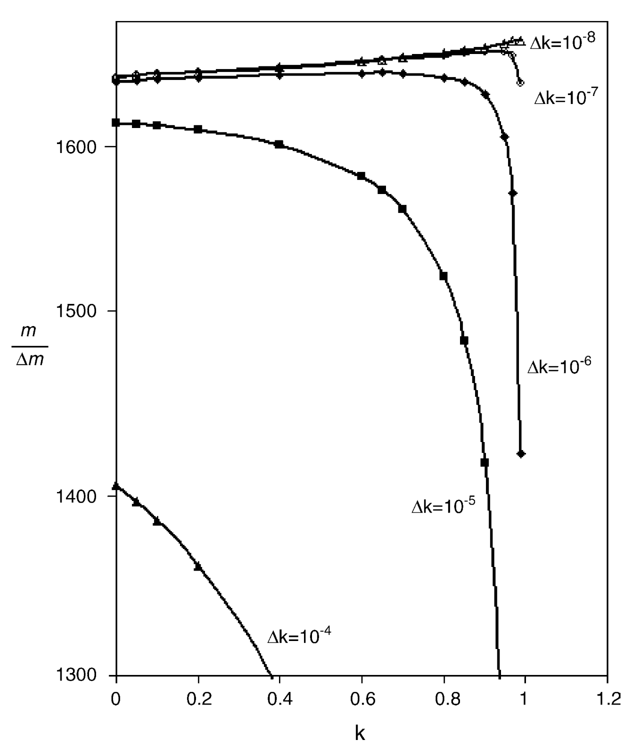

Fig. 7. The fractional resolution as a function of the modulation "index" parameter k.

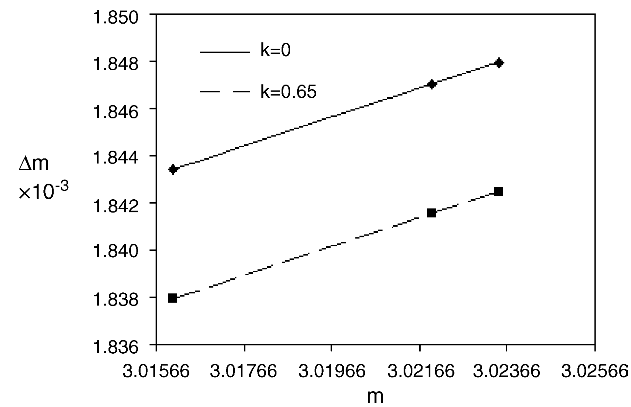

Fig. 8. Resolution of the Paul trap Δm as a function of ion mass m.

$\Delta V/V_k = 10^{-5}$ and we have taken arbitrary different uncertainties values for the modulation "index" parameter Δk such as 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7} and 10^{-8}. From Fig. 7, it can be seen that, the mass resolution for $k = 0.99$ is higher than $k = 0$ when the value of uncertainty Δk is small (10^{-7}, 10^{-8}). This seems to be unrealistic because, in practice it is difficult to amplify equally all the Fourier-components of the voltage signal. Instead, for the present technology, some values less then 10^{-6} seems to be more realistic.

However, from the results obtained in Fig. 7, a fractional resolution of $m/\Delta m = 1636$ for $k = 0$ and $m/\Delta m = 1641$ for $k = 0.65$ was found when $\Delta k = 10^{-6}$. Also, in Fig. 8, we have shown the mass resolution Δm for $H_3^+ = 3.02348$, $HD^+ = 3.02193$, $^3He^+ = 3.01603$ and with $k = 0$, $k = 0.65$ and $\Delta k = 10^{-6}$. Lower Δm for the impulsional signal is shown which means that, experimentally the width of the mass signal spectra is sharper, the sharper FWHM, the better is the mass separation spectra.

4. Conclusion

The use of impulsional voltage for the confinement of ion in the Paul ion trap mass spectrometer investigated here indicate that, this impulsional voltage is not only useful for the ion constant energy injection into the trap, but it has also a potential application to be a good candidate for the high resolution mass spectrometry, in the lower mass range of 1–4 u. The lower ion mass we insisted here because, as long as seven times higher confinement voltage is needed for the $k = 0.99$ than $k = 0$ therefore, for higher ion masses, more confinement voltages are needed, thus it might pose some problems for the amplification of the higher order harmonics in the impulsional voltage. The situation becomes much easier when dialing with light particles confinement. In this case, for the appropriate chosen rf frequency, the impulsional voltage needed to confine particle masses up to $m = 4$ u is accessible for the Paul ion trap.

When calculating the fractional resolution, the variation of ΔV is kept constant and V_k is varied for various index k. It is quit important when choosing higher k value, the form of the voltage signal stays constant during the confinement time, if no it is better to woke with lower k as this effect the resolution very much.

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