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Modulation parametric resonances and their influence on stability diagram structure

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Abstract

The theory of parametric modulation resonance in hyperboloid mass spectrometers is presented. Modulation resonance appears if parameters of the rf signal are periodically modulated. It is shown that modulation parametric resonances are excited within the region of the stable solutions on the quasistability lines corresponding to the stability parameter of the *n*th order, the absolute value of which is equal to 1. In the case where modulation resonance is excited within the stability zone near the quasistability line, bands of unstable solutions (the instability bands) appear. The equations for the maximum value of the instability parameter and for the width of the instability band are presented. The utilization of the modulation parametric resonance for ion analysis is discussed. The relationship between the resolution and the required sorting time is given. The harmonic and the pulse rf signals for the hyperboloid ion trap have been theoretically investigated. The resonance excitation efficiency for parameters of rf signal modulated by a periodic signal of a complicated shape has been obtained. The application of modulation parametric resonance for the hyperboloid mass spectrometers and its prospect for improvement of analytical parameters, in particular, for increase of analysis speed are discussed. (Int J Mass Spectrom 184 (1999) 207–216) © 1999 Elsevier Science B.V.

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1. Introduction

In recent years, resonant excitation of ions has been extensively exploited in hyperboloid[†] mass spectrometry as a powerful technique utilizing a supplementary periodic field.

There are two ways of supplementary field creation: linear and nonlinear. In the first case the field within an analyzer is close to the ideal field with a quadratic distribution of the potential (the forces acting upon a charged particle in each of three perpendicular directions are in proportion to the respective coordinates). Here, ion trajectories can be described by a linear differential equation of the second order (for example, by the Hill equation or by its particular case—the Mathieu equation [1]). The principle of independence of ion oscillations along the coordinate axes can be implemented in such analyzers.

In the second case the field within an analyzer is nonlinear. The force acting upon an ion has some higher harmonics and ion oscillations along the coordinate axes become coupled (which is very important).

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† This term is used to define those mass spectrometers in which the electrode shapes are combinations of one-sheet and/or two-sheet hyperboloids.

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Linear excitation was used for the first time by Paul and co-workers [2]. This mode was achieved by superimposing an additional rf signal on the driving rf signal. Most of the commercial instruments utilize the nonlinear manner. For example, in three-dimensional ion traps a supplementary rf potential difference is usually applied across the endcap electrodes. This dramatically improves parameters of mass spectrometers [3–8]. Further developments of the idea of using a supplementary rf field are in the works [9–12], in which a filtered noise signal was used for excitation.

From our point of view, using the linear field is more preferable because it does not change the linearity of the differential equations, which describe the ion motion. Practically, this manner can be implemented by superimposing a signal of excitation on the driving rf signal, or by modulation of parameters of the rf signal (for instance, in the case of the sine-wave signal, these parameters are: a frequency, an amplitude, and a dc potential). In this article we shall discuss the theory of modulation, which is very easy to apply for the case of a pulsed rf signal.

2. Quasistability lines

When the basic rf signal without any modulation is applied to electrodes of a hyperboloid mass spectrometer then the projections of ion trajectories on the coordinate axes can be defined by the Hill equations. Generally speaking, parameters of these equations for different axes are different, but they correspond to the canonical form, which is given by

$$\ddot{y} + y\psi(t) = 0 \tag{1}$$

where $\psi(t)$ is a periodic function of period T_0.

The parameter of stability $\nu(1)$ depends on $\psi(t)$, and this dependence, in turn, defines the configuration of the stability diagram. On the boundaries of the stability diagram the value of $\nu(1)$ is equal to $|1|$. Within the region of stable solutions $|\nu(1)| < 1$, and within the unstable region $|\nu(1)| > 1$.

If we rewrite the general solution (1) as

$$y(t_0, t) = y_0\psi_1(t_0, t) + \dot{y}_0\psi_2(t_0, t)$$

where y_0 and $\dot{y}_0$ are, respectively, the initial coordinate and velocity, and t_0 is its start time, then for $\nu(1)$ we have [1]

$$2\nu(1) = \psi_1(t_0, t_0 + T_0) + \dot{\psi}_2(t_0, t_0 + T_0) \tag{2}$$

Index "1" in our definition of the stability parameter $\nu(1)$ has the meaning that this parameter is defined only on one period T_0 of the function $\psi(t)$. But nT_0 (where n is an integer) also is a period of $\psi(t)$. Thus we can consider $\nu(n)$ as stability parameter of the nth order and express it as analogous to Eq. (2):

$$2\nu(n) = \psi_1(t_0, t_0 + nT_0) + \dot{\psi}_2(t_0, t_0 + nT_0) \tag{3}$$

It can be shown that in the stability region $\nu(n)$ and $\nu(1)$ are related as follows:

$$\nu(n) = \cos n \ \arccos \nu(1) \tag{4}$$

On the stability boundaries $|\nu(1)| = 1$, and therefore $|\nu(n)| = 1$. Although, within the stability region $|\nu(1)| < 1$, whereas $|\nu(n)|$ can be equal to 1.

Let us call the lines inside the stability zone, for which $|\nu(n)| = 1$, quasistability lines (QSLs). We can see that the function $\nu(n) = f(\nu(1))$ has extreme points on the QSLs. This is the difference between QSLs and stability boundaries, on which the derivative of $\nu(n)$ with respect to $\nu(1)$ is not zero. There are $n - 1$ lines of quasistability for each n. The QSLs do not usually affect ion motion if the $\psi(t)$ signal is undistorted. But even a small disturbance of $\psi(t)$ by the periodic signal of period nT_0 exactly on the line of quasistability with the respective n can lead to $|\nu(n)| > 1$, which makes the motion of ions unstable (and a band of instability appears near the QSL). The QSL can be interpreted as the "rolled-up" zones of instability and "ready to expand" under the coincident influence on the $\psi(t)$ function. As was demonstrated in [13–15] several improvements in parameters of hyperboloid mass spectrometers (HMS) can be made by changing the $\psi(t)$ function shape, which changes the shape of the general stability diagram. In this article we shall try to discuss the prospects of conversion of the stability zones by "excitation" of the QSLs.

3. The general equation

When the driven rf signal modulated by a supplementary signal is applied to the electrodes of the HMS (here, we consider amplitude modulation) then for a low modulation level the Hill equation can be expressed in the following form:

$$\ddot{y} + y\psi(t)[1 + \epsilon_0\varphi(t)] = 0 \tag{5}$$

where $\psi(t)$ has period of T_0, and $\varphi(t)$ has period of nT_0, $\epsilon_0 \ll 1$ and amplitude of $\varphi(t)$ is close to 1 (this limitation is not strict). The general solution of Eq. (5) can be expressed in the form of series expansion

$$y(t) = y_0(t) + \epsilon_0 y_{01}(t) + \epsilon_0^2 y_{02}(t) + \cdots$$

Substituting this (sequence) expansion into Eq. (5) and assigning zero to coefficients near ϵ_0^n we obtain the following system of equations (the Poisson method):

$$\begin{aligned} &\ddot{y}_0(t) + \psi(t)y_0(t) = 0 \\ &\qquad \ddot{y}_{01} + \psi(t)y_{01}(t) = -\psi(t)\varphi(t)y_0(t), \\ &\qquad \cdots \\ &\qquad \ddot{y}_{0i}(t) + \psi(t)y_{0i}(t) = -\psi(t)y_{0_{i-1}}(t) \end{aligned} \tag{6}$$

This system is solved in succession [1]:

$$y_{0i}(t) = A_i y_1(t) + B_i y_2(t) - \frac{1}{\gamma}\left[\begin{array}{l} y_1(t)\displaystyle\int y_2(t)y_{0_{i-1}}(t)\psi(t)\varphi(t)\,dt \\ -\,y_2(t)\displaystyle\int y_1(t)y_{0_{i-1}}(t)\psi(t)\varphi(t)\,dt \end{array}\right]$$

Here $y_1(t)$ and $y_2(t)$ are two independent partial solutions of original equation (5) defined with $\epsilon = 0$; γ is the Wronskian determinant of the same equation.

For $i > 0$, we can find A_i and B_i from the following conditions: when $t = t_0$, $y_{0i}(t = t_0) = 0$ and $\dot{y}_{01}(t = t_0) = 0$. For $i = 0$, we can find A_i and B_i from the following conditions: when $t = t_0$, $y_0(t = t_0) = y_0$ and $\dot{y}_0(t = t_0) = \dot{y}_0$. Thus, for $\nu(n)$ we obtain

$$2\nu(n) = k_0 + \epsilon_0 k_1 + \cdots + \epsilon_0^i k_i + \cdots \tag{7}$$

where

$$k_i = [y_{0i_{(1,0)}}(t_0 + nT_0) + \dot{y}_{0i_{(0,1)}}(t_0 + nT_0)]$$

$y_{0i_{(1,0)}}(t)$ is defined for $y_0 = 1$ and $\dot{y}_0 = 0$;
$\dot{y}_{0i_{(0,1)}}(t)$ is defined for $y_0 = 0$ and $\dot{y}_0 = 1$.

For the first three coefficients k_i we obtain the general expressions

$$k_0 = \alpha_1(n) + \beta_2(n)$$

$$k_1 = \frac{1}{\gamma}\int_{t_0+nT_0}^{t_0} \cdot \left\{\begin{array}{l} [\alpha_1(n) - \beta_2(n)]y_1(t)y_2(t) \\ +\,\alpha_2(n)y_2^2(t) - \beta_1(n)y_1^2(t) \end{array}\right\}\psi(t)\varphi(y)\,dt$$

$$k_2 = \frac{1}{\gamma_0^2}\int_{t_0+nT_0}^{t_0} \cdot \left\{\begin{array}{l} \phi_{1,2}(t)\left\{\begin{array}{l}[\alpha_1(n) + \beta_2(n)]y_1(t)y_2(t) \\ -\,\alpha_2(n)y_2^2(t) - \beta_1(n)y_1^2(t)\end{array}\right\} \\ +\,\phi_{2,2}(t)[\alpha_2(n)y_1(t)y_2(t) - \beta_2(n)y_1^2(t)] \\ +\,\phi_{1,1}(t)[\beta_1(n)y_1(t)y_2(t) - \alpha_1(n)y_2^2(t)] \end{array}\right\} \psi(t)\varphi(t)\,dt \tag{8}$$

$$\phi_{1,2}(t) = \int_t^{t_0} y_1(t)y_2(t)\psi(t)\varphi(t)\,dt$$

$$\phi_{1,1}(t) = \int_t^{t_0} y_1^2(t)\psi(t)\varphi(t)\,dt$$

$$\phi_{2,2}(t) = \int_t^{t_0} y_2^2(t)\psi(t)\varphi(t)\,dt$$

where $\alpha_1(n)$, $\alpha_2(n)$, $\beta_1(n)$, and $\beta_2(n)$ are coefficients defined from

$$y_1(t + nT_0) = \alpha_1(n)y_1(t) + \alpha_2(n)y_2(t)$$

$$y_2(t + nT_0) = \beta_1(n)y_1(t) + \beta_2(n)y_2(t)$$

Eqs. (7) and (8) are the solutions of the problem in the general form: we have found the stability parameter

for modulation of the $\psi(t)$ function with the $\varphi(t)$ signal.

4. Harmonic signal

Now consider the solution of the problem for the Mathieu equation (harmonic signal). In this case [1]

$$y_1(t) = \sum_{-\infty}^{+\infty} C_{2r} \cos\,(2r + \beta)t$$

$$y_2(t) = \sum_{-\infty}^{+\infty} C_{2r} \sin\,(2r + \beta)t$$

$$\alpha_1(n) = \cos\,\beta n\pi$$

$$\alpha_2(n) = -\sin\,\beta n\pi$$

$$\beta_1(n) = \sin\,\beta n\pi$$

$$\beta_2(n) = \cos\,\beta n\pi$$

$$T_0 = \pi$$

For k_i we have

$$k_0 = 2\cos\,\beta n\pi$$

$$k_1 = -\frac{1}{\gamma}\sin\,\beta n\pi \int_{t_0+n\pi}^{t_0} [y_1^2(t) + y_2^2(t)]\psi(t)\varphi(t)\,dt$$

$$k_2 = \frac{1}{\gamma^2}\cos\,\beta n\pi \int_{t_0+n\pi}^{t_0} \cdot \begin{bmatrix} 2\phi_{1,2}(t)y_1(t)y_2(t) \\ -\phi_{2,2}(t)y_1^2(t) - \phi_{1,1}(t)y_2^2(t) \end{bmatrix} \cdot \psi(t)\varphi(t)\,dt + \frac{1}{\gamma^2}\sin\,\beta n\pi \cdot \int_{t_0+n\pi}^{t_0} \begin{bmatrix} \phi_{1,2}(y_2^2(t)-y_1^2(t)) \\ +(\phi_{1,1}(t)-\phi_{2,2}(t))y_1(t)y_2(t) \end{bmatrix} \cdot \psi(t)\varphi(t)\,dt \quad (9)$$

and for $\nu(n)$ confined to the first three terms of the expansion we obtain

$$\nu(n) = \left[1 + \frac{\epsilon_0^2}{2\gamma_0^2} C_0\right]\cos\,\beta n\pi + \frac{\epsilon_0}{2\gamma_0} D_0 \sin\,\beta n\pi \quad (10)$$

where C_0 and D_0 are the respective integrals in Eq. (9).

From this general expression we can draw several important conclusions: (1) when $C_0 > 0$ on a line of quasistability then a given $\varphi(t)$ signal excites this line, near which a band of instability appears; (2) a width of the instability band can be approximately estimated as

$$\Delta\beta_n \cong 2\,\frac{\epsilon_0}{\gamma_0 n\pi}\,d_0^{1/2}$$

$$d_0 = C_0 + \left(\frac{D_0}{2}\right)^2$$

where $\Delta\beta_n$ is a width of the instability band defined as the difference between the values of β on its boundaries. The value of $\Delta\beta_n$ can be interpreted as a value inversely proportional to the resolution across the stability zone, because the value of β varies up to 1 within this zone. In this case the resolution within instability band can be estimated as

$$\rho = \rho_z \frac{1}{\Delta\beta_n}$$

where ρ_z is the resolution for the zone surrounding the working point, and can be defined as the value inverse to the relative width of this zone. Thus, in the case of the ion trap, in the mode where $a = 0$, $\rho_z \approx 0.5$; near the apex of the first stability zone the resolution is increased up to 2 to 3. (1) When $D_0 \neq 0$ the extreme point of $\nu(n)$ within the instability band is not located in its center. If $D_0 = 0$ it can be taken that the extreme point of $\nu(n)$ lies on the line of quasistability. (2) The maximum value of $\nu(n)$ within the instability band can be expressed as

$$\nu(n)_{\max} \cong \left[1 + \frac{\epsilon_0^2}{\gamma_0^2}\,d_0\right]^{1/2}$$

If μ is a parameter of instability [1] then we obtain

$$\mu^2 \cong \frac{\epsilon_0^2 d_0}{\gamma_0^2 (n\pi)^2}$$

and the relation between $\Delta\beta_n$ and μ:

$$\Delta\beta_n = 2\mu$$

(3) Using equations for $\Delta\beta_n$ and μ obtained previously and evaluating N_{sort} from

$$\mu N_{\text{sort}}\pi = \ln(1/\Delta)$$

we can find

$$N_{\text{sort}} = \frac{2\ln(1/\Delta)}{\pi\rho_z}\rho$$

If we accept $\Delta_0 = 0.1$ and $\rho_z = 0.5$ ($a = 0$) we obtain

$$N_{\text{sort}} = 2.93\rho$$

and if we want to increase the resolution in the mass-selective instability mode ($a = 0$) by using a band of instability, we need almost 300 periods of rf field in order to reach $\rho = 100$ and $\Delta_0 = 0.1$. At the same time, it follows from the formula of Paul and co-workers [2]

$$N_{\text{sort}} \approx 3.5\rho^{1/2}$$

that the same resolution can be obtained about 10 times faster. The sorting time can be decreased by 4 to 6 times if the ion trap operates within the instability band near the apex of the first common stability zone. But this time is still greater then the sorting time in the apex of this zone (in this case the time defined in [16] gives $N_{\text{sort}} = 25$). The resolution ρ_z is increased up to 25 to 30 and the sorting time within the instability band is decreased to several periods if the ion trap operates in the upper stability zones. It should be noted that the estimation we carried out implies the continuous exposure of the excitement field. The influence of this field can be increased if it is turned on not immediately after the forming of ions in the trap.

Let us consider the modulation signal in the following form:

$$\varphi(t) = \cos 2\Omega t$$

where $\Omega = p/n$; p is a nonzero integer.

Then we have

$$D_0 = 0$$

$$C_0 = \frac{(n\pi)^2}{32}\sum_{-\infty}^{+\infty} {}^2C_{2r}C_{-2(r+\eta)}[-2(r+\eta)+\beta]^2 \tag{11}$$

where $\eta = \beta \pm \Omega$.

In the case of the sine-wave signal for the coefficient C_0 we obtain the same expression. Since η may have only two values (0 and 1), coefficient C_0 also has two values. It means that one harmonic signal simultaneously excites two lines of quasistability, which correspond to $\beta = 1 - \Omega$ and $\beta = \Omega$, respectively. The signal of frequency $\Omega = 0.5$ excites only one line of quasistability with $\beta = 0.5$. As follows from Eq. (11), the efficiency of the QSL excitement is different for different lines and the same lines can be excited by different signals with the different efficiency (we mean that the values of C_0 are different).

For example, we have found the values of C_0 for the working point, which lies on the working line with $a = 0$ (frequently used in the mass-selective mode). In this case $q = 0.4511$ and $\beta = 1/3$. This line of quasistability can be excited by the harmonic signal with $\Omega_1 = 1/3$ and $\Omega_2 = 2/3$. The sum of series in Eq. (11) is equal to 0.25 in the case of Ω_1 and equal to 0.48 in the case of Ω_2. Since the sum in Eq. (11) is squared, the line of quasistability corresponding to $\beta = 1/3$ ($n = 3$) is excited by the signal of frequency $\Omega_2 = 2/3$ more effectively than by the signal of frequency $\Omega_1 = 1/3$. For the Mathieu equation, as we have shown [Eq. (5)], the modulation mode implies the modulation of a dc potential and a rf potential by one signal simultaneously. In practice, however, the modulation of one parameter can be obtained.

When only a dc potential is modulated by the signal $\cos 2\Omega t$ we obtain the following expression for C_0:

$$C_0 = \frac{(n\pi)^2}{32}a^2\sum_{+\infty}^{-\infty} {}^2C_{2r}C_{-2(r+\eta)} \tag{12}$$

When only a rf amplitude is modulated:

$$C_0 = \frac{(n\pi)^2}{32} q^2 \sum_{+\infty}^{-\infty} {}^2C_{2r}[C_{-2(r+1+\eta)} + C_{-2(r-1+\eta)}] \tag{13}$$

When only a phase is modulated:

$$C_0 = \frac{(n\pi)^2}{32} q^2 \sum_{+\infty}^{-\infty} {}^2C_{2r}[C_{-2(r+1+\eta)} - C_{-2(r-1+\eta)}] \tag{14}$$

When the whole signal is modulated by a complicated function, for instance, by

$$\varphi(t) = \sum_{i=0}^{i_0} b_i \cos 2\Omega_i t$$

then for evaluation of C_0 one obtains the following expression:

$$C_0 = \frac{(n\pi)^2}{32} \cdot \left\{ \sum_{i=0}^{i_0} b_i \sum_{-\infty}^{+\infty} C_{2r} C_{-2(r+\eta)}[-2(r+\eta)+\beta]^2 \right\}^2 \tag{15}$$

Here Ω_i limits i_0:

$$\Omega_{i0} \leq 1.$$

As follows from the numerical calculation using the equations obtained that the modulation efficiencies of different parameters significantly differ (the value of the stability parameter is defined by C_0). The modulation of an amplitude corresponding to $\beta = 1/3$, $a = 0$, and $q = 0.4511$ by a signal of frequency $\Omega = 2/3$ yields the value of C_0 three and a half times greater then for modulation by a signal with $\Omega = 1/3$. The modulation of a phase obtained with $\Omega = 2/3$ yields the value of C_0 about 40 times greater than in the case of $\Omega = 1/3$. When $\beta = 2/3$, $a = 0$, and $q = 0.7847$ the modulation parametric resonance can be excited either by $\Omega = 1/3$ or $\Omega = 2/3$. Here the values of C_0 are almost the same.

The modulation by a signal that is described by an odd function does not change Eq. (15).

If we assume for the ion trap the working time of one cycle is of $\sim 10^2$ periods then the equations obtained give us the value of ϵ_0 such that the amplitude of motion of ions, whose working point lies within a band of instability, will increase by a factor of 2. As it turned out, $\epsilon_0 < 1\%$ is sufficient for such considerable increasing of the ion amplitude. Thus, even a small excitation signal can effectively excite the lines of quasistability, which dramatically increases the amplitude of the ions and ejects them from the ion trap. This decreases the sensitivity of the analyzer and causes the mass peak shape to deteriorate.

5. Pulse signal

Using a pulse signal can also excite the modulation parametric resonance in HMS. In this case, the modulation function should also be pulsed. If we apply the conventional bipolar signal, which consists of two signals of different polarity, for different duration and amplitude, we can modulate (simultaneously or separately) the pulse amplitude, the period of pulse function, or the relative pulse duration (the pulse width high to pulse width low ratio).

A period of the modulation function can be taken as equal to n periods of the working pulse signal. We can also assume that one of the signal parameters has a fixed value for n_1 periods, and for n_2 periods it has another value ($n_1 + n_2 = n$). We note, however, that it is not quite correct to speak here about "the pulse modulation function." For example, when we modulate the relative pulse duration, it is more pertinent to speak about timing features of this modulation.

In the theory of the pulse signal for the HMS it is more comfortable to use the pulse parameters [13]:

$$a_i^2 = \frac{2\Delta U_i T_0^2 e}{m\chi_j d^2},$$

where e/m is the charge-to-mass ratio; T_0 is a period of the pulse function; χ_j is the geometrical parameter of the electrode system; d is the characteristic dimension of the electrode system; ΔU_i is the potential

difference between electrodes corresponding to a given pulse signal; and $2d$ is the closest distance between the two endcap electrodes along the y axis.

For the elliptic electrode system [17]:

$$\chi_x = 1 + n_0 + p_0$$

$$\chi_y = \frac{1 + n_0 + p_0}{p_0}$$

$$\chi_z = -\frac{1 + n_0 + p_0}{1 + p_0}$$

For the axisymmetric ion trap:

$$\chi_r = 2 + n_0 \qquad \chi_z = -\frac{2 + n_0}{2}$$

For the electrode system of the quadrupole mass filter: $d = r_0$ is a radius of the field; $\chi_x = 2$; $\chi_y = -2$.

The coordinate of an ion is usually normalized to the characteristic geometrical dimension, and the velocity is normalized to a period T_0. In this case the dimensionless velocity and coordinate of an ion before the pulse field exposure and after are related to each other with elements of the transformation matrix [13]:

$$\dot{y}(t_0 + T_0) = \psi_1(t_0)y_0 + \psi_2(t_0)\dot{y}_0$$

$$y(t_0 + T_0) = \psi_3(t_0)y_0 + \psi_4(t_0)\dot{y}_0$$

where t_0 is the phase where the initial parameters y and $\dot{y}$ are being set up. Keeping in mind that the elements of the transformation matrix depend on t_0, we can omit t_0 henceforth.

We have obtained the following expression:

$$2\nu(n) = 2\cos\bar{\omega}n_1\cos\omega n_2 + \left[\begin{array}{l}\psi_1\bar{\psi}_4 + \psi_4\bar{\psi}_1 + \psi_2\bar{\psi}_2 \\ \quad + \psi_3\bar{\psi}_3 - 2\nu(1)\bar{\nu}(1)\end{array}\right]\frac{\sin\bar{\omega}n_1\sin\omega n_2}{\sin\bar{\omega}\sin\omega} \qquad (16)$$

where $\cos\omega = \nu(1)$, and an overbar means that the value of this parameter is changed by modulation.

Let us simplify the problem: we put $n_1 = 1$, and therefore $n_2 = n - 1$. So long as ψ_i, $\nu(1)$, and ω are the multivariable functions, the values of $\bar{\psi}_i$, $\bar{\nu}(1)$, and $\bar{\omega}$ can be obtained by using the Taylor approximation for a multivariable function. When the level of modulation is low enough for $\nu(n)$, and two parameters are modulated simultaneously, then we obtain

$$\nu(n) = [1 + \varphi(i, j)]\cos\omega n + \psi(i, j)\sin\omega n \qquad (17)$$

where

$$\varphi(i, j) = \frac{1}{2}\left\{\begin{array}{l}(\Delta i)^2\left[\frac{\partial\psi_1}{\partial i}\frac{\partial\psi_4}{\partial i} - \frac{\partial\psi_2}{\partial i}\frac{\partial\psi_3}{\partial i}\right] \\ + (\Delta i)(\Delta j)\left[\frac{\partial\psi_1}{\partial j}\frac{\partial\psi_4}{\partial i} + \frac{\partial\psi_1}{\partial i}\frac{\partial\psi_4}{\partial j}\right/ \\ \qquad - \frac{\partial\psi_3}{\partial i}\frac{\partial\psi_2}{\partial j} - \frac{\partial\psi_3}{\partial j}\frac{\partial\psi_2}{\partial i} \\ + (\Delta j)^2\left[\frac{\partial\psi_1}{\partial j}\frac{\partial\psi_4}{\partial j} - \frac{\partial\psi_2}{\partial j}\frac{\partial\psi_3}{\partial j}\right]\end{array}\right\}$$

$$\psi(i, j) = -\left[\frac{\partial\omega}{\partial i}(\Delta i) + \frac{\partial\omega}{\partial j}(\Delta j)\right]$$

For the extreme value of $\nu(n)_m$ within the instability band:

$$\begin{aligned}\nu^2(n)_m = 1 &+ (\Delta i)^2\left[\frac{\partial\psi_1}{\partial i}\frac{\partial\psi_4}{\partial i} - \frac{\partial\psi_2}{\partial i}\frac{\partial\psi_3}{\partial i} + \left(\frac{\partial\omega}{\partial i}\right)^2\right] \\ &+ (\Delta i)(\Delta j)\left[\frac{\partial\psi_1}{\partial j}\frac{\partial\psi_4}{\partial i} + \frac{\partial\psi_1}{\partial i}\frac{\partial\psi_4}{\partial j}\right/ \\ &\quad - \frac{\partial\psi_3}{\partial i}\frac{\partial\psi_2}{\partial j} - \frac{\partial\psi_3}{\partial j}\frac{\partial\psi_2}{\partial i} + 2\frac{\partial\omega}{\partial i}\frac{\partial\omega}{\partial j} \\ &+ (\Delta j)^2\left[\frac{\partial\psi_1}{\partial j}\frac{\partial\psi_4}{\partial j} - \frac{\partial\psi_2}{\partial j}\frac{\partial\psi_3}{\partial j} + \left(\frac{\partial\omega}{\partial j}\right)^2\right]\end{aligned} \qquad (18)$$

It can be seen from Eq. (17) that the point on the stability diagram that corresponds to the extreme value of $\nu(n)_m$ for $\psi(i, j) \neq 0$ is shifted from the respective line of quasistability. This is the distinctive feature of the instability band structure for the HMS utilizing the rf pulse signal.

The elements of the transformation matrix are given by

$$\psi_1 = a_i sha_i\delta_i cha_j\delta_j + a_j sha_j\delta_j cha_i\delta_i$$

$$\psi_2 = cha_i\delta_i cha_j\delta_j + \frac{a_j}{a_i} sha_i\delta_i sha_j\delta_j \quad (19)$$

$$\psi_3 = cha_i\delta_i cha_j\delta_j + \frac{a_i}{a_j} sha_i\delta_i sha_j\delta_j$$

$$\psi_4 = \frac{1}{a_i} sha_i\delta_i cha_j\delta_j + \frac{1}{a_j} sha_j\delta_j cha_i\delta_i$$

For some modulations of the working signals Eq. (18) can be simplified. For example, if only one parameter is modulated, Eq. (18) includes the first two terms only. There is a possibility to modulate the relative pulse duration by increasing the duration of one pulse and decreasing the other in the same value during one period (the common period is a constant). Then Eq. (18) can be transformed into the following form:

$$\nu^2(n)_m = 1 + \frac{1}{4}(\Delta\delta)^2(a_i^2 - a_j^2)^2 \frac{\psi_4^2}{1 - \nu^2(1)} \quad (20)$$

A width of the instability band in the case of the pulse signal is given by

$$\Delta\omega_{\text{inst}} \cong \frac{2}{n}[\psi^2(j, i) + 2\varphi(j, i)]^{1/2} \quad (21)$$

and when the relative pulse duration is modulated [see Eq. (20)]:

$$\Delta\nu(1)_{\text{inst}} = \left|\frac{\Delta\delta(a_i^2 - a_j^2)\psi_4}{n}\right| \quad (22)$$

It is interesting to note, that a width of the instability band does not depend on $\nu(1)$. The dependence of the sorting time on the resolution is similar to that we have obtained for the harmonic signal:

$$N_{\text{sort}} = \ln(1/\Delta)[1 - \nu^2(1)]^{1/2}\rho/\rho_z \quad (23)$$

where N_{sort} is the number of sorting periods. It should be noted that Eq. (23) includes

$$[1 - \nu^2(1)]^{1/2}.$$

This means that for the instability bands located close to a boundary of the common stability zone, the required sorting time is reduced and the respective ions leave the electrode system faster.

6. Stability diagram modification

Modulation parametric resonance, with its instability bands appearing in the stability zones, has attractive prospects for the mass-selective ejection of ions from the ion trap. The basic theoretical principles of such selective separation have been shown. But, the instability bands are broadened with an increase of modulation level, and as follows from the equations obtained, the stability zones are transformed into the narrow stability zones and the common stability zone turns into several small zones separated by instability zones. Under the circumstances we have the opportunity to use these narrow stability zones for the one-dimensional sorting of the charged particles, advantages which we have previously reported. In this case the sorting process can be carried out "along the boundary" of the instability band. This mode of operation is traditionally used in hyperboloid mass spectrometry. The sorting efficiency of the charged particles depends on the structure of the instability region directly adjacent to the boundary of the stability zone. In particular, the changing of the "sorting" parameter μ [1] within this boundary region is very important. For practical mass spectrometry the relationship between the desired sorting time and the resolution level [see, for instance, Eq. (23)] is very important. The above theory yields the equation describing the boundaries of the instability band caused by the modulation parametric resonance.

The dependence of ρ on N_{sort} can be expressed as

$$\rho = \rho_z \frac{c_{00} + (c_{00}^2 + \ln^2(1/\Delta)/N_{\text{sort}}^2]^{1/2}}{[1 - \nu^2(1)]^{1/2}\ln^2(1/\Delta)} N_{\text{sort}}^2 \quad (24)$$

where

$$c_{00} = \frac{1}{n}\{\psi^2(i, j) + [1 + \varphi(i, j)]^2\}^{1/2}$$

From this equation two important conclusions follow. When the modulation is not significant then

$$[\psi(i, j)^2 + [1 + \varphi(i, j)]^2 - 1] \to 0,$$

and Eq. (24) can be changed to Eq. (23).

When the modulation is significant, and the instability bands are transformed into the broad zones of unstable solutions and Eq. (24) becomes

$$N_{\text{sort}} \cong \left[\frac{\ln^2(1/\Delta)[1-\nu^2(1)]^{1/2}n}{2\rho_z\{\psi^2(i,j)+[1+\varphi(i,j)]^2-1\}^{1/2}}\right]^{1/2}\rho^{1/2} \quad (25)$$

We can see that the required sorting time in Eq. (23) is increased proportionally to the resolution; in Eq. (25) this dependence has been changed. Here the sorting time is increased in proportion to $\rho^{1/2}$, which is typical for HMS operating near the stability diagram boundaries. This remarkable property decelerates the increasing N_{sort} when ρ is significant and allows one to develop the high-speed hyperboloid mass spectrometers with high resolution. Although, as we can see from Eq. (25), an increase of n also increases $\nu(1)$, which is not rational. A more attractive option is to change the width of the instability band, and respectively, the width of the working stability band by variation of the modulation level of the respective parameter.

It can be demonstrated that for $\Delta\delta \sim 15\%$ the value of the coefficient before $\rho^{1/2}$ is 3 times less than the value calculated from the Paul et al. formula for the quadrupole mass filter. This is a substantial argument in favor of one-dimensional sorting in the first zone of the stability diagram.

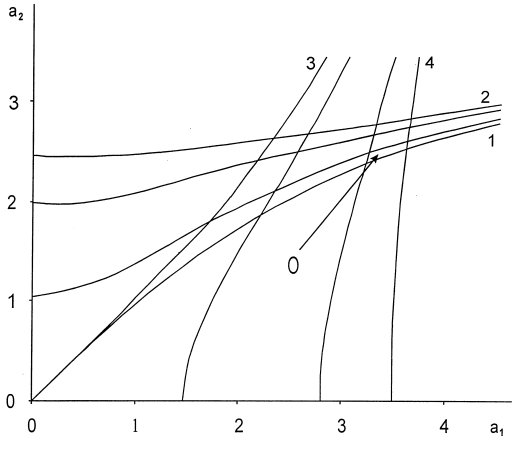

Fig. 1. The common stability diagram of axially symmetric ion trap for parameters a_1 and a_2 modulated by 2%. 1 – $\nu_z(1) = 1$; 2 – $\nu_z(1) = -1$; 3 – $\nu_r(1) = 1$; 4 – $\nu_r(1) = -1$.

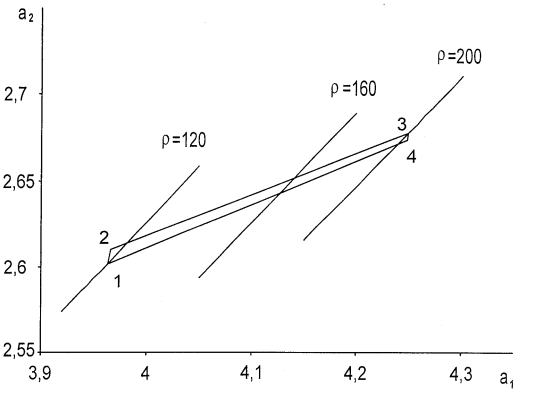

Fig. 2. The small stability zone (labeled "O" in Fig. 1) for parameters a_1 and a_2 modulated by 20%.

The common stability diagram modified by instability bands is shown in Fig. 1 for the axially symmetric ion trap as an example of modulation parametric resonance when $n = 3$. The parameters a_1 and a_2 were modulated. The modulation level was 2% for both parameters. As a result of the modulation the first common stability zone is divided into the six smaller zones: two zones per each coordinate. The configuration of the smaller zone (labeled "O" in Fig. 1) for the modulation level of 20% for the same parameters a_1 and a_2 is demonstrated in Fig. 2. The working lines and the respective resolutions are shown. For this zone the values of parameters a_1 and a_2 are presented in Table 1.

We have found that the value of $\omega\rho^{1/2}$ is a constant along the working line for different resolutions (from 10 to 15 up to several thousands) for zone showed in Fig. 2. We calculated the slope angle of the working line for the point lying deep inside this zone ($\lambda = 0.639\,541\,09$). We obtained the different values of $\omega\rho^{1/2}$ for two boundaries of the stability zone. For the

Table 1
The values of parameters a_1 and a_2 corresponding to apexes of the small zone

Number of apex	1	2	3	4
a_1	3,9636	3,9658	4,2488	4,2482
a_2	2,6019	2,6096	2,6775	2,6733

side lying close to the origin of coordinates $\omega\rho^{1/2} = 8$, and for the opposite side $\omega\rho^{1/2} = 8.6$. The value of $\omega\rho^{1/2}$ for the z boundary near the upper apex of common stability zone for three-dimensional axially symmetric ion trap is less than or equal to 3. Thus, it decreases the number of sorting periods almost 2.5 times for a constant resolution near the instability band. This is particularly important for the development of new instruments with high analysis speed.

7. Conclusions

In this article (1) we have developed the theoretical principles of parametric modulation resonance in the hyperboloid mass spectrometer; some special features of modulation by continuous and discrete signals (harmonic and pulse signals for HMS) have been investigated; the equations for the width of instability bands and for the extreme value of the instability parameter within the bands have been obtained; the relationship between the resolution and the required sorting time have been found for the HMS utilizing modulation resonances; (2) we have shown that the modulation of the rf signal parameters by a complex signal causes the interference of influence of their harmonics; it has been demonstrated that such interference may appear by simultaneous modulation of two different parameters of the rf signal; (3) it has been shown that the modulation parametric resonance using a harmonic signal excites two quasistability lines, near which instability bands appear; (4) the common stability diagram is extremely sensitive to the modulation parametric resonance; for doubling of oscillation amplitude for ions, which working points lie within the instability band, during the sorting time, the modulation of 1% for a parameter of rf signal is sufficient; (5) it has been demonstrated that modulation parametric resonance can be successfully used for the intentional modification of the common stability zones: the modulation of 20% for the pulse signal transforms the first stability zone into the set of narrow instability bands and provides effective one-dimensional sorting.

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