Ideal Velocity Focusing in a Reflectron Time-of-Flight Mass Spectrometer

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A single-stage ion mirror in a time-of-flight (TOF) mass spectrometer (MS) can perform first order velocity focusing of ions initially located at a start focal plane while second order velocity focusing can be achieved using a double-stage reflectron. The situation is quite different when an ion source extraction field is taken into account. In this case which is common in any practical matrix-assisted laser desorption/ionization (MALDI) TOF-MS a single-stage reflectron, for example, cannot perform velocity focusing at all. In this paper an *exact*, *analytic* solution for an electric field inside a one-dimensional reflectron has been found to achieve universal temporal focusing of ions having an initial velocity distribution. The general solution is valid for arbitrary electric field distributions in the upstream (from the ion source to the reflectron) and downstream (from the reflectron to an ion detector) regions and in a decelerating part of the reflectron of a reflectron TOF mass spectrometer. The results obtained are especially useful for designing MALDI reflectron TOF mass spectrometers in which the initial velocity distribution of MALDI ions is the major limiting factor for achieving high mass resolution. Using analytical expressions obtained for an arbitrary case, convenient working formulas are derived for the case of a reflectron TOF-MS with a dual-stage extraction ion source. The special case of a MALDI reflectron TOF-MS with an ion source having a low acceleration voltage (or large extraction region) is considered. The formulas derived correct the effect of the acceleration regions in a MALDI ion source and after the reflectron before detecting ions. (J Am Soc Mass Spectrom 1999, 10, 992–999) © 1999 American Society for Mass Spectrometry

The time-of-flight (TOF) mass spectrometer (MS) is a simple instrument in which ions are accelerated to the same energy and allowed to drift along some path before detection. Because ions of different mass have different velocities after acceleration they are separated in space during flight and in time during detection; thus, the time of arrival to the detector is a measure of mass (or mass-to-charge ratio *m/z* if ions are not singly charged). However, such a simple picture is always complicated by the presence of nonideal factors, among them [1]: (a) different time of formation or acceleration of ions; (b) different initial locations of ions in space; and (c) different initial velocities of ions before acceleration. Time focusing can be achieved by using pulsed drawout fields with sharp rise times or short laser pulses in the case of laser desorption (LD) or matrix-assisted laser desorption/ionization (MALDI). A dual-stage extraction method is normally used for correction of the initial spatial distribution of ions in an ion source [2]. And finally, initial velocity (or energy) distribution can be corrected partially by a time-lag focusing technique which is now also referred to as pulsed, delayed or time-delayed extraction [2–6].

In this work we consider only the compensation of the initial velocity distribution of ions that is motivated primarily by the wide use of MALDI and LD-TOF instruments. Since MALDI and LD ions are desorbed from or formed near a well-defined smoothed surface of a conductor the initial spatial distribution of ions is minimized. Initial temporal distribution for ions is also very small due to the use of short pulse lasers (the pulse width of a nitrogen laser is usually less than 1 ns). Thus, among the above sources resulting in broadening the mass spectral lines the initial velocity distribution is of primary concern. MALDI ions, for example, are desorbed with mean velocities up to hundreds of meters per second that depend primarily on the matrix, and the energy of desorbed ions may easily reach 10–100 eV depending on ion mass [7–12].

The single, but major drawback of using time-delayed extraction for initial velocity distribution correction is that it is mass dependent [2] which is problematic for a TOF mass spectrometer intended to record the entire mass range simultaneously. A number of investigators have produced improvements in time-delayed extraction techniques and other methods using dy-

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1044-0305/99/$20.00
PII S1044-0305(99)00067-7

Received February 4, 1999
Revised April 26, 1999
Accepted April 30, 1999

namic electric fields [13–20]; however, the problem of mass dependence in the case of using pulsed extraction fields is far from being resolved.

Alternatively, an approach to mass independent compensation for the initial velocity distribution of ions has been possible with the invention of the ion mirror or the reflectron [21]. A reflectron does not actually make a correction of the initial spatial, temporal, or velocity distributions and, in fact, the temporal, spatial, and velocity distributions at the start focal plane are transferred to the target focal plane formed after reflection but with some distortion. If the initial velocity distribution is a major limiting factor in increasing the mass resolution then the accuracy of such transfer by the reflectron is usually expressed by the *order of velocity focusing* which is actually the power of the highest zero term in the expansion of the ion time-of-flight dependence over the initial ion velocity. For example, a single-stage linear reflectron performs first order velocity focusing, whereas a two-stage linear reflectron can focus with second order accuracy [21]. A parabolic mirror [22] can perform infinite order focusing, i.e., the ion TOF does not depend on the initial kinetic energy of ions at all. Such mirrors are also referred to as *ideal* reflectrons. The field inside a parabolic reflectron is curved along the axis and according to the LaPlace equation it also has a curvature in a radial (or transverse) direction. This, of course, limits the angular aperture of such a reflectron, or otherwise divergent ions will have different kinetic energy resulting in lower mass resolution. An additional potential drawback of the parabolic reflectron is that it does not have a field-free region which is generally required in TOF-MS for mounting detectors, lenses, energy filters, etc. This drawback is overcome in another design for an ideal reflectron [23] in which a nonlinear field is also used inside the reflectron but the field-free path can be made any length in comparison with the reflectron length if the minimum initial energy of ions to be focused is allowed to be larger than zero (a parabolic reflectron focuses ions of all energies starting from zero). The authors [23] obtained the most general solution for the field inside such an ideal reflectron. Solutions for some special cases have also been reported using analytical [24] and numerical [25] approaches.

Thus, when a reflectron is introduced the problem of velocity focusing is reduced to obtaining good conditions at the start focal plane. This is not a problem if the initial spatial distribution in the ion source makes a major contribution to the line broadening in the mass spectra because any single- or double-stage extraction scheme effectively eliminates the ion space distribution (converting it into the larger velocity distribution of ions at the focal plane). In the case of MALDI where the major contribution into the line broadening comes from the initial velocity distribution of ions the situation is not so clear. It has been shown that the velocity focusing cannot be achieved at all in a MALDI/TOF-MS with a single-stage reflectron [26]. The use of very high acceleration voltages facilitates but does not solve the problem completely. The problem of velocity focusing in a MALDI/TOF-MS can be solved with a specially designed double-stage reflectron [26, 27] but the order of accuracy of the velocity focusing is limited.

In this work the problem of ideal (or infinite order) velocity focusing in a reflectron TOF mass spectrometer is solved in a one-dimensional approximation. The work may be considered as the generalization of the problem of designing the ideal reflectron [23] which in addition to a field-free region includes also acceleration and deceleration fields always present in any TOF-MS. Analytic expressions obtained in our work are valid for arbitrary electric field distributions in an upstream region (from the ion source to the reflectron) and downstream region (from the reflectron to an ion detector) as well as in the deceleration region of the reflectron. The field in the correcting part of the reflectron is determined by the electric field distributions in the upstream region, the deceleration part of the reflectron, and the downstream region of TOF-MS. Then, the properties of the general solutions are studied for the common case of linear acceleration/deceleration fields in the upstream and downstream regions and low acceleration voltage (or long extraction region) used in an ion source.

Theoretical Approach

In this work the problem of the ideal velocity focusing of ions is solved for a whole TOF-MS system which may include ion source acceleration regions, a field-free region, a reflectron, energy discrimination filters, post-source acceleration before ion detection, etc. The task is formulated for a one-dimensional model in the most general case, i.e., for ions initially formed at the start plane in an ion source with full (kinetic plus potential) energy within an interval from V_0 to V, to determine a field inside the reflectron which would perform infinite order velocity focusing at the detector plane. The ion potential energy $U_u(x)$ due to the electric field in the upstream region (from the ion source to the reflectron) can be different from that $U_d(x)$ in the downstream region (from the reflectron to an ion detector) as shown in Figure 1. For simplicity the potential energy at the entry to the reflectron is taken as a reference point equal to zero. In addition to the upstream and downstream regions the potential energy $U_r(x)$ inside the reflectron from zero up to V_0 can also be arbitrary. Thus, the potential field $V_r(x)$ from V_0 to V in the correcting part of the reflectron shown by the dashed line in Figure 1 is to be found. Note that the situation is quite different from that when only linear fields inside the TOF-MS are considered [26, 27]. In the latter case the field inside the reflectron *and* the upstream (and/or downstream) region should be determined to achieve first (or higher) order velocity focusing. In our case we determine

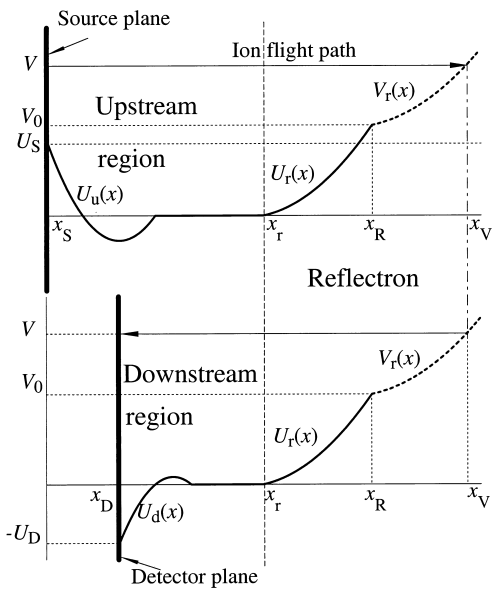

Figure 1. A schematic presentation of the ion potential energy during an ion flight from an ion source to a detector via the upstream region, the reflectron, and the downstream region of a TOF-MS.

infinite order velocity conditions for the arbitrary potential fields $U_u(x)$ and $U_d(x)$ in the upstream and downstream regions and even for the arbitrary field $U_r(x)$ in the decelerating part of the reflectron. This becomes possible because the potential field $V_r(x)$ which is to be found can be curved, i.e., it is determined by the infinite number of parameters. This, of course, does not preclude optimizing the fields $U_u(x)$, $U_r(x)$, and $U_d(x)$. As can be shown these fields can be chosen to facilitate the solution of other tasks such as tuning and building the reflectron.

The total TOF t for an ion of mass m and the full (potential plus kinetic) energy ϵ can be written as

$$\bar{t} = \int_{x_S}^{x_r} \frac{dx}{\sqrt{\epsilon - U_u(x)}} + \int_{x_D}^{x_r} \frac{dx}{\sqrt{\epsilon - U_d(x)}} + 2\int_{x_r}^{x_R} \frac{dx}{\sqrt{\epsilon - U_r(x)}} + 2\int_{x_R}^{x_\epsilon} \frac{dx}{\sqrt{\epsilon - V_r(x)}} \quad (1)$$

where x_ϵ is defined by $V_r(x_\epsilon) = \epsilon$; and $\bar{t} = t\sqrt{2/m}$ is a reduced TOF. The first and the second terms of the right side of this equation are the TOF for the upstream and downstream regions correspondingly, the third and the fourth terms correspond to the flight forward and back through the decelerating and correcting parts of the reflectron, respectively.

In the case of linear fields in a reflectron TOF-MS [26, 27] formula 1 for the TOF t is normally expressed as a series expansion over the initial ion velocity $\nu_S = \sqrt{2(\epsilon - U_S)/m}$, where U_S is the initial potential energy of the ion (see Figure 1) and, then, the parameters of the linear electric fields are tuned to make the expansion terms responsible for the first (or higher) order velocity focusing equal to zero. In our case the time t does not depend upon the ion initial energy within the interval from V_0 to V and the function $V_r(x)$ should be found by solving the integral equation 1.

Results and Discussion

Solution of the Integral Equation for the General Case

To solve the integral equation 1 we use the method similar to that described previously [23]. After multiplying both sides of equation 1 by $1/2\pi\sqrt{V - \epsilon}$ and integrating over ϵ from V_0 to V (see Figure 1) one can obtain

$$\Delta x_V = \frac{1}{\pi}\,\bar{t}(V_0\bar{V})^{1/2} - J_u - J_d - 2J_r \quad (2)$$

where $\bar{V} = (V - V_0)/V_0$ is a dimensionless potential in the second part of the reflectron;

$$\Delta x_V = \frac{1}{\pi}\int_{V_0}^{V} d\epsilon \int_{x_R}^{x_\epsilon} \frac{dx}{\sqrt{(V-\epsilon)[\epsilon - V_r(x)]}}$$
$$= \frac{1}{\pi}\int_{x_R}^{x_V} dx \int_{V_r(x)}^{V} \frac{d\epsilon}{\sqrt{(V-\epsilon)[\epsilon - V_r(x)]}}$$
$$= \frac{1}{\pi}\int_{x_R}^{x_V} dx\left[-\arctan\left(\frac{V - 2\epsilon + V_r(x)}{2\sqrt{(V-\epsilon)[\epsilon - V_r(x)]}}\right)\right]\Bigg|_{V_r(x)}^{V}$$
$$= x_V - x_R \quad (3)$$

where for arbitrary function $f(\epsilon)$ we defined $f(\epsilon)|_b^a = f(a) - f(b)$;

$$J_a = \frac{1}{2\pi}\int_{V_0}^{V} d\epsilon \int_{x_a}^{x_A} \frac{dx}{\sqrt{(V-\epsilon)[\epsilon - U_a(x)]}}$$
$$= \frac{1}{2\pi}\int_{x_a}^{x_A} dx \int_{V_0}^{V} \frac{d\epsilon}{\sqrt{(V-\epsilon)[\epsilon - U_a(x)]}}$$
$$= \frac{1}{2\pi}\int_{x_a}^{x_A} dx\left[-\arctan\left(\frac{V - 2\epsilon + U_a(x)}{2\sqrt{(V-\epsilon)[\epsilon - U_a(x)]}}\right)\right]\Bigg|_{V_0}^{V}$$
$$= \frac{1}{\pi}\int_{x_a}^{x_A} dx \arctan\sqrt{\frac{\bar{V}}{\bar{U}_a(x)}} \quad (4)$$

where $\bar{U}_a = [V_0 - U_a(x)]/V_0$; $a = u, d,$ or r; x_a and x_A are the limits of the action of the corresponding potential, e.g., $(x_a, x_A) = (x_S, x_r)$ and $(x_a, x_A) = (x_D, x_r)$ for the cases $a = u$ and d correspondingly. We used the trigonometric identity $\arctan[(1/x - x)/2] = \pi/2 - 2\arctan(x)$ to derive the final result 4.

Equation 2 determines the coordinate x_V at which the potential in the correcting part of the reflectron is equal to V, i.e., it determines in reciprocal fashion the function $V = V_r(x)$.

Note that $\bar{t}$ in eq 2 is an arbitrary parameter. Limits for this parameter will be discussed later. Let us designate

$$\bar{t}_0 = \int_{x_S}^{x_r} \frac{dx}{\sqrt{V_0 - U_u(x)}} + \int_{x_D}^{x_r} \frac{dx}{\sqrt{V_0 - U_d(x)}} + 2\int_{x_r}^{x_R} \frac{dx}{\sqrt{V_0 - U_r(x)}} \tag{5}$$

Then, the solution 2 can be rewritten as

$$\Delta x_V = \frac{(\bar{t} - \bar{t}_0)V_0^{1/2}}{\pi} \bar{V}^{1/2} - I_u - I_d - 2I_r \tag{6}$$

where

$$I_a = \frac{1}{\pi}\int_{x_a}^{x_A} dx\left(\arctan\sqrt{\frac{\bar{V}}{\bar{U}_a(x)}} - \sqrt{\frac{\bar{V}}{\bar{U}_a(x)}}\right) \tag{7}$$

where the definitions for a and limits of the integration are the same as in integral 4.

Properties of the General Solution in the Case $V_0 \neq U_s$

Let us consider the behavior of the solution function 6 near the point $x = x_R$. Although this is not absolutely necessary for our analysis we assume (and this is true for the majority of the practical cases) that the function $\bar{U}_a(x)$ is not equal to zero except the point x_R and may be the start point in the ion source x_S. The latter is possible only in the case $V_0 = U_S$ and is considered below.

In the vicinity of $x = x_R$ we may take into account only the linear dependence of the function $\bar{U}_r(x)$ which we define as $\bar{U}_r(x) = \bar{U}'(x_R - x)/\Delta x_R$, where $\bar{U}' \ll 1$, $\Delta x_R \ll 1$. The integral 7 in the case $a = r$ can be presented as

$$I_r = I'_r + I''_r \tag{8}$$

where

$$I'_r = \frac{1}{\pi}\int_{x_r}^{x_R - \Delta x_R} dx\left(\arctan\sqrt{\frac{\bar{V}}{\bar{U}_r(x)}} - \sqrt{\frac{\bar{V}}{\bar{U}_r(x)}}\right) \tag{9}$$

$$I''_r = \frac{1}{\pi}\int_{x_R - \Delta x_R}^{x_R} dx\left[\arctan\sqrt{\frac{\bar{V}}{\bar{U}_r(x)}} - \sqrt{\frac{\bar{V}}{\bar{U}_r(x)}}\right] = \frac{\Delta x_R V'}{\pi}\int_0^{1/V'} d\nu\left[\arctan\sqrt{\frac{1}{\nu}} - \sqrt{\frac{1}{\nu}}\right] = \frac{\Delta x_R}{\pi}\left[\arctan\sqrt{V'} - \sqrt{V'} - \frac{\pi V'}{2} + V'\arctan\sqrt{V'}\right] \tag{10}$$

where $V' = \bar{V}/\bar{U}'$. We used substitution $\nu = \bar{U}_r(x)/\bar{V}$ during integration to obtain the final expression 10. For small V' one can expand the expression 10 in the series

$$I''_r = \frac{\Delta x_R}{\pi}\left[-\frac{\pi V'}{2} + \frac{2}{3}V'^{3/2} + \cdots\right] \tag{11}$$

In the cases $a = u$ and d and $\bar{V} \ll 0$ the expression under the integral 7 can also be expanded in a series that results in

$$I_a = \frac{1}{\pi}\int_{x_a}^{x_A} dx\left[-\frac{1}{3}\left(\frac{\bar{V}}{\bar{U}_a(x)}\right)^{3/2} + \frac{1}{5}\left(\frac{\bar{V}}{\bar{U}_a(x)}\right)^{5/2} - \cdots\right] \tag{12}$$

After integration the integral 12 contains only the terms proportional to $\bar{V}^{3/2}$, $\bar{V}^{5/2}$, and higher order terms. A similar expression (with different integration limits) can be obtained for the integral 9. Thus, the integrals 12 and 9 do not contain low order terms with $\bar{V}^{1/2}$ and $\bar{V}$. The only low order term in the integral 6 is from the expression 11 and the final result for the case $\bar{t} = \bar{t}_0$ can be written as

$$\Delta x_V = \Delta x_R V' + aV'^{3/2} + bV'^{5/2} + \cdots \tag{13}$$

where a and b are some coefficients. One can see that the electric field in the *second* part of the reflectron is linear near the point $x = x_R$ and

$$E_V = E_r \tag{14}$$

where E_V and E_r are the absolute values for the electric field strength near the point $x = x_R$ in the second (correcting) and first (decelerating) parts of the reflectron, respectively.

Properties of the General Solution in the Case $U_S = V_0$

In this case the integral I_u also makes a contribution to the low order terms in the solution 6. The expression for the integral I_u can be calculated similarly to I_r by taking into account only the linear part of the function $\bar{U}_u(x) = \bar{U}'(x - x_S)/\Delta x_S$ near the point $x = x_S$:

$$I_u = I'_u + I''_u \tag{15}$$

where

$$I'_u = \frac{1}{\pi}\int_{x_S+\Delta x_S}^{x_r} dx\left[\arctan\sqrt{\frac{\bar{V}}{\bar{U}_u(x)}} - \sqrt{\frac{\bar{V}}{\bar{U}_u(x)}}\right] \tag{16}$$

$$I''_u = \frac{1}{\pi}\int_{x_S}^{x_S+\Delta x_S} dx\left[\arctan\sqrt{\frac{\bar{V}}{\bar{U}_u(x)}} - \sqrt{\frac{\bar{V}}{\bar{U}_u(x)}}\right]$$

$$= \frac{\Delta x_S}{\pi}\left[\arctan\sqrt{V'} - \sqrt{V'} - \frac{\pi V'}{2} + V' \arctan\sqrt{V'}\right]$$

$$= \frac{\Delta x_S}{\pi}\left[-\frac{\pi V'}{2} + \frac{2}{3}V'^{3/2} + \cdots\right] \tag{17}$$

Because, similar to the integral 12 the integrals I'_u, I'_r, and I_d in solution 6 do not contain low order terms with $\bar{V}^{1/2}$ and $\bar{V}$, the integrals 10 and 17 only generate low order terms. Similar to expression 13 one can obtain for the case $\bar{t} = \bar{t}_0$:

$$\Delta x_V = \left(\frac{1}{2}\Delta x_S + \Delta x_R\right)V' + aV'^{3/2} + bV'^{5/2} + \cdots \tag{18}$$

that results in the following relation between electric field strengths:

$$\frac{1}{E_V} = \frac{1}{2E_s} + \frac{1}{E_r} \tag{19}$$

where E_S is the absolute value of the electric field strength near the start plane in the source region ($x = x_S$). Formula 19 can be considered as a generalization of the result obtained for the case of linear electric fields [26]. Thus, the electric field potential near $x = x_R$ in the reflectron always has a cusp if ions of all velocities (starting from zero) in the ion source are to be focused.

Limits for the Parameter $\bar{t}$

As mentioned previously, the parameter $\bar{t}$ is an arbitrary parameter in this theory. If the ion full energy ϵ in eq 1 is equal to $V_0(\epsilon = V_0)$ then two cases may occur: (a) the last term in the right side of eq 1 is equal to zero; or (b) the last term is not equal to zero. In the latter case (b) $\bar{t}$ must be larger than $\bar{t}_0$ because otherwise Δx_V in the solution 6 can become negative and the potential inside the reflectron cannot be defined unambiguously. The situation in case (b) is very similar to that of a parabolic mirror in which the TOF is a finite value (greater than zero) even for zero entrance energy [22]. This results in terms proportional to $(\bar{V})^{1/2}$ in the solutions 2 or 6. In case (a) $\bar{t} = \bar{t}_0$ and the terms proportional to $(\bar{V})^{1/2}$ are not present in the solutions 2 and 6 as follows from our previous results 8–13 and 15–18. One can obtain, similar to expression 18, an expansion valid near the point $x = x_R$:

$$\Delta x_V = \frac{(\bar{t} - \bar{t}_0)V_0^{1/2}}{\pi}\bar{V}^{1/2} + \Delta x\bar{V} + A\bar{V}^{3/2} + B\bar{V}^{5/2} + \cdots \tag{20}$$

where Δx, A, B, etc. are the expansion coefficients.

Thus, only the values of $\bar{t} \geq \bar{t}_0$ are allowed and the quadratic term is always present in the correcting part $V_r(x)$ of the reflectron if $\bar{t} > \bar{t}_0$. The choice $\bar{t} = \bar{t}_0$ is the only opportunity to avoid the quadratic term in the correcting part of the reflectron. Quadratic fields are practically difficult to design whereas there are no major problems for generating a linear field near $x = x_R$ in the case $\bar{t} = \bar{t}_0$.

Low Acceleration Voltage Case

The acceleration voltage can be comparable to the energy of ions formed in an ion source especially in the case of high mass MALDI ions [7–12] and when a double-stage extraction scheme is used. This is the case which is most suitable for applying the theory because linear fields inside the reflectron do not provide the necessary accuracy for velocity focusing or do not focus at all [26]. One more reason to consider the low acceleration case is that in a conventional reflectron TOF-MS the length of the second correcting part of the reflectron would be too small and comparable to the distance between the wires in meshes commonly used for building grids in the reflectrons. This is not desirable because of the large deflection of ions passing through the mesh in this case [28], the subsequent distortion of ion trajectories and its effect on the ion TOF.

In one example we consider a TOF-MS with a dual-stage linear extraction field ion source, a linear deceleration part of the reflectron, and a linear acceleration region before ion detection (Figure 2). We have chosen the double-stage extraction scheme because it is much easier to tune the potential GV_0 on the middle acceleration grid (G is the geometrical factor shown in Figure 2) than to fit geometrical parameters of the system to get optimum operation. The case $\bar{t} = \bar{t}_0$ is considered as the most practical.

In the case of linear variation of the potential energy function $U_a(x)$ from U_1 to U_2 on the interval $\Delta x_a = x_2 - x_1$ the integral 7 can be directly calculated:

$$I_a = \frac{\Delta x_a \bar{V}}{\pi \Delta \bar{U}_a}\left[F\left(\frac{\bar{V}}{\bar{U}_2}\right) - F\left(\frac{\bar{V}}{\bar{U}_1}\right)\right] \tag{21}$$

where $\bar{U}_i = (V_0 - U_i)/V_0(i = 1 \text{ or } 2)$, $\Delta\bar{U}_a = \bar{U}_2 - \bar{U}_1$, and

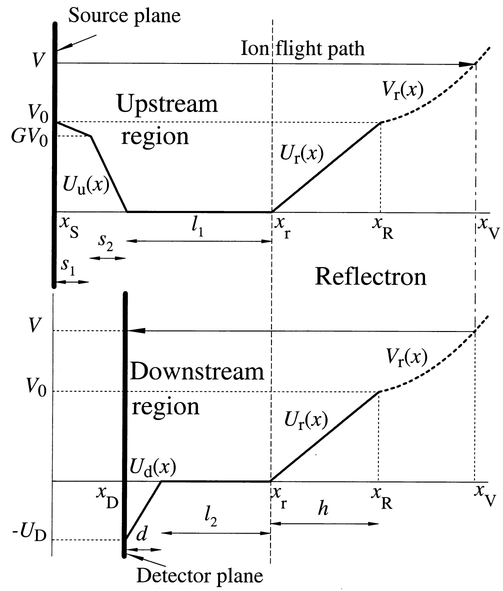

Figure 2. A schematic presentation of the potential energy profile with a double-stage ion extraction used in the case of low acceleration voltage.

$$F(u) = \frac{1}{u}\arctan\sqrt{u} - \frac{1}{\sqrt{u}} + \arctan\sqrt{u} \tag{22}$$

The dependence $F(u)$ is shown in Figure 3. In the case of field-free region one can obtain for the integral 7

$$I_a = \frac{\Delta x_a}{\pi}\left[\arctan\sqrt{\frac{\bar{V}}{\bar{U}_a}} - \sqrt{\frac{\bar{V}}{\bar{U}_a}}\right] \tag{23}$$

Using the expressions 21 and 23 in solution 6 for the case shown in Figure 2 one can obtain

$$\Delta x_V = \left[\frac{s_1}{2(1-G)} + h\right]\bar{V} - \left[\frac{s_2}{G} + 2h - \frac{V_0 d}{U_D}\right]\frac{\bar{V}}{\pi}F(\bar{V})$$

$$-\left[\frac{s_1}{1-G} - \frac{s_2}{G}\right]\frac{\bar{V}}{\pi}F\left(\frac{\bar{V}}{1-G}\right)$$

$$-\frac{V_0 d}{U_D}\frac{\bar{V}}{\pi}F\left(\frac{\bar{V}}{1+U_D/V_0}\right) - \frac{L}{\pi}\left[\arctan\sqrt{\bar{V}} - \sqrt{\bar{V}}\right] \tag{24}$$

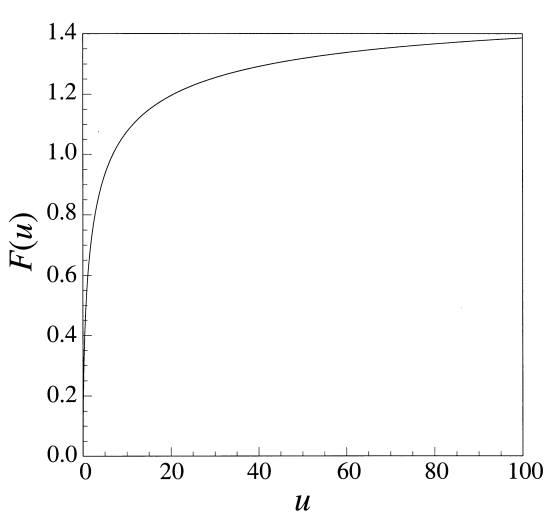

Figure 3. The function $F(u)$ determined by eq 22 which is used in the formula for the integral eq 21.

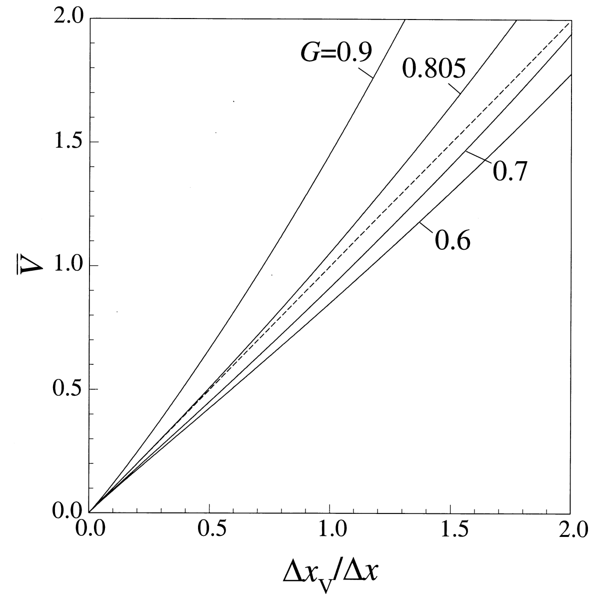

Figure 4. The ideal velocity focusing potential in the correcting part of the reflectron for the special case of the potential distribution shown in Figure 2 and the different values of the parameter G (see text for details).

where $L = l_1 + l_2$; l_1 and l_2 are the lengths of the field-free paths in the upstream and downstream regions respectively; s_1 and s_2 are the extraction and acceleration interval lengths in the ion source; h is the length of the deceleration region of the reflectron; d is the length of the acceleration region before ion detection (see Figure 2 for geometry definitions); U_D is the acceleration potential before ion detection.

Calculations have been performed for a small size TOF-MS that is typical for a low acceleration voltage instrument: $L = 30$ cm, $s_1 = s_2 = 1$ cm, $h = 2.5$ cm, $d = 1$ cm, $U_D/V_0 = 50$. The ideal velocity focusing potential profiles in the second correcting part of the reflectron against the coordinate variable of $\Delta x_V/\Delta x$ where $\Delta x = h + s_1/2(1 - G)$ are shown in Figure 4 for different values of G. Note that in comparison with the linear field case [26] where the ion velocity can be focused only for some specially tuned geometrical parameters in our case there is always a curved field solution for any parameter G. In the coordinates of Figure 4 the slope of the potential curves near $\Delta x_V/\Delta x = 0$ is not dependent of the parameter G and is equal to that of the dashed line shown in Figure 4.

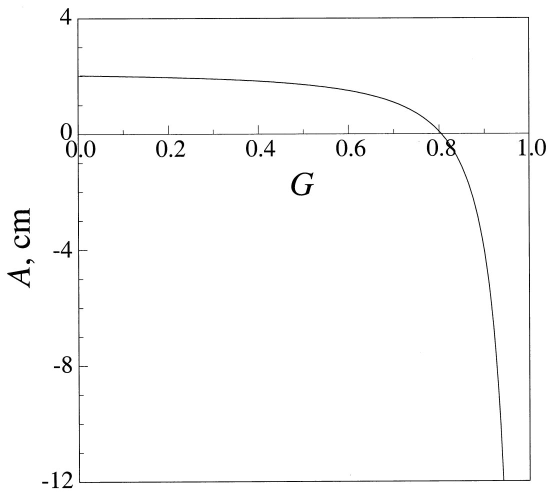

Figure 5. The dependence of the expansion paramter A in the formula eq 20 upon the parameter G of the ion source extraction region for the special case of the potential distribution shown in Figure 2 (see text for details).

Special Case of the Correcting Field Close to Linear Field

One can see that the curvature of the reflectron correction field in Figure 4 is determined by the geometrical properties of TOF-MS, in this case by the parameter G which determines the extraction and acceleration fields in the double-stage ion source. Of course, it is possible to adjust the geometrical factor G to obtain the correction field in the reflectron as close to a linear one as possible. The more linear solution for the correction part of the reflectron the easier to implement it in practice. To achieve this goal it is required to make the expansion terms of power higher than unity in the formula 20 equal to zero. In our case we have just one parameter (G) to adjust and, thus, we will need to zero the term containing $\bar{V}^{3/2}$ only. Using the expression 24 for Δx_V one can obtain the expansion coefficient A in the formula 20

$$A = \frac{2}{3\pi}\left[\frac{L}{2} - \frac{s_2}{G} - 2h + \frac{V_0 d}{U_D} - \frac{1}{\sqrt{1-G}}\left(\frac{s_1}{1-G} - \frac{s_2}{G}\right) - \frac{1}{\sqrt{1 + U_D/V_0}}\frac{V_0 d}{U_D}\right] \quad (25)$$

The dependence of A upon the factor G is shown in Figure 5. One can see that A is equal to zero at $G \approx 0.805$. For this G the potential inside the correction part of the reflectron shown in Figure 4 is really very close to the line, at least in the interval $0 < \Delta x_V/\Delta x < 0.4$. This means that the linear field in the correcting part of the reflectron can effectively focus ions with the initial kinetic energy up to 40% of the acceleration potential V_0. According to Figure 4 this interval is much smaller if $G \neq 0.805$. Thus, using our theory one can choose the geometry of a TOF-MS to achieve a more linear potential in the correcting part of the reflectron. In the case considered one parameter was adjusted to cause the coefficient A to vanish in the expansion formula 20. It is clear that by diminishing the next term coefficient B in the formula 20 one can get even more linear potential inside the correcting part of the reflectron. This may take place if additional parameters in TOF-MS are allowed to *be* tune. These parameters may arise if, for example, additional stages in the ion source or the reflectron are taken into consideration.

Conclusions

The potential inside the reflectron described by eq 6 can perform ideal focusing of the ion velocity in a reflectron TOF-MS. Note that the general formula 6 for the correcting reflectron field exists for arbitrary geometry and potential fields in *the* upstream and downstream regions and in a decelerating part of the reflectron of a reflectron TOF-MS. This is because the potential field inside the reflectron is not linear and, thus, is effectively described by an infinite number of parameters. However, the curvature of the correcting potential field depends on the geometry of the accelerating fields in the ion source as well as in the postacceleration region before ion detection. This fact can be used for minimizing the potential distribution curvature to facilitate reflectron construction. MALDI/TOF-MS is seen as the primary field for the application of the theory because the initial velocity distribution of MALDI ions is the major limiting factor in achieving high mass resolution. Simple working formulas have been obtained for the most practical case of a TOF instrument with the two-stage ion source/two-stage reflectron. Similar formulas for designing a reflectron TOF-MS can be easily obtained for any other cases.

Acknowledgments

This work was supported in part by a grant from the National Institutes of Health (R01 RR08912) and carried out at the Middle Atlantic Mass Spectrometry Laboratory.

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