The linear mass reflectron

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(Submitted 2 December 1977; resubmitted 3 October 1978)
Zh. Eksp. Teor. Fiz. 76, 1500–1505 (May 1979)

A description of the design and operation is given for the linear mass reflectron—a new nonmagnetic time-of-flight mass spectrometer with high resolution. An experimental study of the instrument is reported. For an ion drift length of 0.6 m the instrument has a resolution of about 1200 in the width of the peaks at half-height. This design makes possible a construction of mass-spectrometer probes of small size with high resolution and sensitivity.

PACS numbers: 07.75. + h

INTRODUCTION

Time-of-flight mass spectrometers are finding extensive application in various physical and chemical investigations as the result of such advantages as unlimited mass range, high speed, and panoramic view of the mass spectrum. However, the modest resolution (no more than a few hundred) has substantially limited the applicability of these instruments.

In previous articles[1-4] we have reported on a new nonmagnetic time-of-flight mass spectrometer with substantially increased resolution—the mass reflectron with a V-shaped ion trajectory. With acceptable geometrical and electrical parameters the resolution of the device reaches 3000 in the width of the mass peaks at half-height. This device has a certain deficiencies: the necessity that the plane of the ion packets be perpendicular to the chamber axis but not to the ion velocity vector; the difficulty of focusing the ion beam in the angles of emission of ions from the source with a V-shaped trajectory; the increased diameter of the analyzer chamber.

As the result of further investigation we have suggested[5,6] a new system of ion optics for the mass reflectron—the linear mass reflectron.

DESCRIPTION AND PRINCIPLE OF ACTION OF THE APPARATUS

The principle of operation of the linear mass reflectron, like that of the instrument with V-shaped ion trajectory, consists of compensation of the difference in times-of-flight of ions of different energies over a field-free region by means of a system of electrostatic fields which result in focusing of the ion packets in space and time at the detector entrance plane. In the linear mass reflectron (Fig. 1) the ions move along trajectories parallel to the axis of the analyzer chamber, and therefore the new scheme does not involve the deficiencies listed above for the instrument with the V-shaped ion trajectory.

The formation of ion packets in the linear mass reflectron occurs as follows. Ions produced in the ionization chamber d_1 of the source S are extracted from it by a rectangular voltage pulse U_1, accelerated in the first accelerating gap d_5, pass through the first field-free drift space L_1, are reflected in the reflector REF (the gaps d_3 and d_4), pass through the drift space L_1 and the source in the reverse direction and the second drift space L_2, and hit the detector D. The total time of motion of the ions from the starting point to the detector can be divided into two parts: T_1 is the time of motion in the reflector and T_2 is the time of motion in the remaining portions. As they traverse the entire path except the reflector, ions with a given mass-to-charge ratio but with higher energies expend less time than ions with lower energy. The ions with higher energies moving in the reflector are reflected from deeper equipotential planes and are in the reflector a greater time than ions with low energies. The reflector parameters can be chosen in such a way that the total time $T = T_1 + T_2$ expended in the apparatus by ions with a given mass-to-charge ratio from the starting point to the detector will be a weak function of their energy. It is evident that if this condition is satisfied ions of a given type will arrive at the detector entrance in the form of a short packet, as is required for attainment of high resolution.

The resolution of such an ion-optical system can be defined by the formula

$$R = T/2\Delta t, \tag{1}$$

where Δt is the duration of the ion packets in the detector entrance plane and T is the time of motion of the ions in the system, which is

$$T = \left(\frac{m}{2q}\right)^{1/2}\left[\frac{2d_1}{U_1}\left(U_1\frac{x}{d_1}\right)^{1/2} + \frac{2d_2}{U_2}\left(\left(U_1\frac{x}{d_1}+U_2\right)^{1/2} - \left(U_1\frac{x}{d_1}\right)^{1/2}\right) + \frac{4d_3}{U_3}\left(\left(U_1\frac{x}{d_1}+U_3\right)^{1/2} - \left(U_1\frac{x}{d_1}+U_3-U_3\right)^{1/2}\right) + \frac{4d_4}{U_4}\left(U_1\frac{x}{d_1}+U_3-U_3\right)^{1/2} + \frac{4d_5}{U_5}\left(\left(U_1\frac{x}{d_1}+U_5\right)^{1/2} - \left(U_1\frac{x}{d_1}\right)^{1/2}\right) + \frac{2L_1}{(U_1x/d_1+U_5)^{1/2}} + \frac{L_2}{(U_1x/d_1+U_2)^{1/2}} + \frac{d_1}{(U_1x/d_1)^{1/2}}\right], \tag{2}$$

where d_i and U_i are respectively the distances and po-

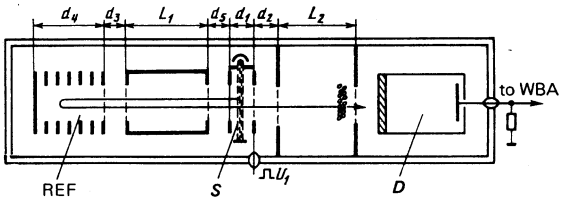

FIG. 1. Diagram of the ion-optical system of the linear mass reflectron. WBA is a wide band amplifier.

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tential differences between the electrodes of the corresponding gaps and x is the path traversed by the ions in the ionization chamber.

The duration Δt of the ion packets at the detector entrance is due to various factors, the most important of which is the spread in initial energies of the ions at the time of application of the extracting voltage pulse. Computer calculations have shown that with optimal adjustment of the system the value of Δt is determined almost completely by the spread ΔU of the initial ion energies and by the parameters of the ionization chamber:

$$\Delta t = \frac{4d_1}{U_1}\left(\frac{m\Delta U}{2q}\right)^{1/2}, \tag{3}$$

where d_1 is the width of the source ionization chamber, U_1 is the height of the extracting voltage pulse, and q and m are respectively the charge and mass of the ion.

It can be seen from Eq. (3) that to reduce the duration of the ion packets at the detector entrance it is necessary to increase as much as possible the height of the extracting pulse and to decrease the width of the ionization chamber. It also follows from the calculations that to obtain maximum resolution of the system the ions must leave the ionization chamber with the greatest possible energy, i.e., the ionization region must be located as close as possible to the electrode on which the extraction pulse is applied. The extent of the ionization region must be reduced as far as possible to a value of the order 0.3–0.5 mm for an ionization chamber width 3–5 mm.

Our analysis showed that the resolution of the ion-optical system of the linear mass reflectron depends only weakly on the size of the gaps d_2, d_3, and d_5 and therefore their widths can be chosen to be on the order of a few millimeters on the basis of mechanical considerations. The accelerating potential differences U_2 and U_5 are best chosen as 2–3 times U_1, depending on the remaining parameters of the device.

The field strength in the reflecting gap can be chosen approximately on the basis of the formula

$$E_4 \approx \frac{8U_2}{2L_1+L_2}. \tag{4}$$

Adjustment of the system is accomplished by choice of the potential U_3 between the electrodes of the first gap of the reflector such that U_3, depending on the remaining parameters of the device, is in the range $(0.6–0.95)U_5$. The depth of the reflecting gap of the reflector must be sufficient for reflection of ions with the maximum energy.

Figure 2 shows plots of R, U_3, and E_4 as a function of the ion drift length $L = 2L_1 + L_2$. The calculations were made for the following parameter values: $U_1 = 300$ V, $U_2 = U_5 = 1000$ V, $d_1 = 2.5$ mm, $d_2 = d_3 = d_5 = 5$ mm, and $\Delta U = 0.1$ eV. The extent of the ionization region along the chamber axis was taken as 0.5 mm, and the ionization region was assumed to be located at a distance 0.5 mm from the electrode to which the extracting pulse is applied.

It can be seen from the plot that the resolution of the

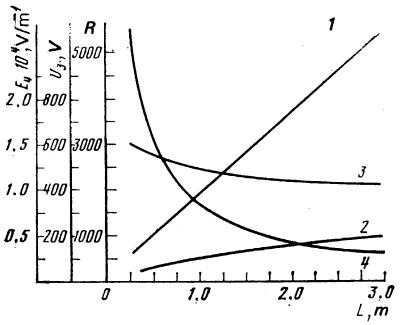

FIG. 2. Resolution of a linear mass reflectron (1), of an ordinary time-of-flight mass spectrometer (2), potential difference between the electrodes of the first gap of the reflector of a linear mass reflectron (3), and field strength in the second gap of the reflector of a linear mass reflectron (4) as a function of ion drift length.

linear mass reflectron depends linearly on the ion drift length and that for equal drift lengths L the resolution for the linear mass reflectron is substantially greater than that for ordinary time-of-flight mass spectrometers. It should also be noted that with location of the source near the detector in the linear mass reflectron the analyzer chamber length can be made considerably less than in ordinary time-of-flight mass spectrometers, as the result of more efficient use of the drift space.

The resolution of the ion-optical system of the linear mass reflectron was calculated without taking into account distortions introduced by the parameters of the detector and recording system, and therefore in estimation of the resolution of the entire apparatus it is necessary to make appropriate corrections.[4,5] To remove the background from ions capable of leaving the source during the interval between extracting voltage pulses it is necessary to use a pulsed ionization mode. The duration of the ionization pulse and the time of application of the extracting pulse must be chosen so as to achieve the greatest sensitivity, and the duration of the extracting pulse must be less than the time of return of the lightest ions studied to the ionization chamber.

Further investigations have shown that various arrangements of the linear mass reflectron are possible (Fig. 3). Decrease of the number of electrodes between the source ionization chamber and the reflecting gap of

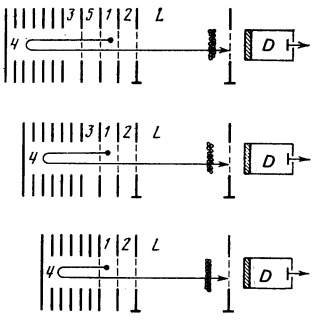

FIG. 3. Versions of the ion-optical system of a linear mass reflectron: 1—source ionization chamber; 2, 5—accelerating gaps; 3, 4—reflector gaps; L—drift space; D—ion detector.

the reflector leads to an increase in the transmission of the ion-optical system, although this reduces somewhat the maximum achievable resolution.

EXPERIMENTAL CHECK OF THE SYSTEM

On the basis of our calculations we constructed and tested an experimental linear mass reflectron. The block diagram of the apparatus is similar to that described previously.[4] The analyzer chamber, constructed of stainless steel, has an overall length 0.9 m and an internal diameter 60 mm. Ionization by electron impact is utilized in the source. The energy of the electrons can be varied from 20 to 200 eV. All parts of the source are made of stainless steel. The electrode apertures are covered with closely spaced grids of palladium-coated copper. The cathode consists of a tungsten wire 150 μm in diameter.

A linear mass reflectron with parameters $L_1 = 20$ mm, $L_2 = 560$ mm, $d_1 = 2.5$ mm, $d_2 = d_3 = d_5 = 5$ mm, $d_4 = 100$ mm, $U_1 = 300$ V, $U_2 = U_5 = 600$ V, $U_3 \approx 500$ V, $E_4 \approx 8000$ V/m, and an ionization region width 0.5 mm (distance from the exit electrode of the ionization chamber 1.5 mm) has a resolution of the order 1200 in the line width at half-height. In Fig. 4 we have shown the mass spectrum of mercurous iodide obtained on the screen of a wide-band oscilloscope, and in the lower trace two neighboring lines with mass numbers 326 and 327. We used the apparatus to study experimentally the analytical characteristics of the linear mass reflectron and their dependence on its geometrical and electrical parameters. When the effect on the resolution of the spread in the angles of emission of the ions from the source, the geometrical depth of the entrance to the secondary-emission multiplier, and the bandwidth of the electronic systems are taken into account, the value of resolution obtained experimentally is in good agreement with that calculated. Comparison of the calculated and measured values showed that for the ion-optical system investigated and with ionization by electron impact in the source it is not necessary to take into account such factors as the space-charge repulsion of the ions in a packet, the distortion of the uniform electric fields near the electrode grids, the presence of a potential well and contact potential difference in the source, and so forth. The linear dependence of the linear mass-reflectron resolution on the ion drift length is confirmed experimentally.

The sensitivity of the linear mass reflection depends on the arrangement chosen and on the drift length of the ions in the device. With the parameters mentioned above, the sensitivity, defined as the minimum partial pressure of one isotope of the analyzed gas in the source for which packets containing on the average one ion reach the detector, is $\approx 10^{-11}$ Torr.

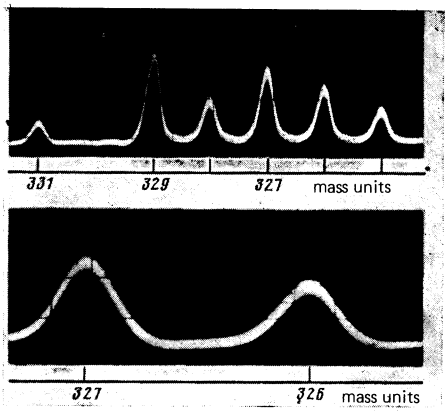

FIG. 4. Oscillograms of the mass spectrum of mercurous iodide (HgI). Below are the lines of $^{199}Hg^{127}I$ and $^{200}Hg^{127}I$.

In the experimental reflectron we investigated versions of the device with different ion drift lengths. The results of tests confirmed the conclusion that the new linear ion-optical system permits construction of an apparatus with substantially greater resolution than in time-of-flight mass spectrometers of the ordinary type with the identical overall size of the analyzer chamber. The existence of various arrangements permits apparatus to be built with different analytical parameters, different constructions, and designs for various uses. It is possible to build mass-spectrometer probes of small size with high sensitivity considerably exceeding that of ordinary time-of-flight mass spectrometers for the same resolution.

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Translated by Clark S. Robinson