The mass-reflectron, a new nonmagnetic time-of-flight mass spectrometer with high resolution

B. A. Mamyrin, V. I. Karataev, D. V. Shmikk, and V. A. Zagulin
A. F. Ioffe Physico-technical Institute, USSR Academy of Sciences
(Submitted July 21, 1972)
Zh. Eksp. Teor. Fiz. **64**, 82-89 (January 1973)

A description and principle of operation are given for the mass-reflection—a new nonmagnetic time-of-flight mass spectrometer with high resolution. The combination of the advantages of a time-of-flight mass spectrometer with high resolution results in important possibilities of the mass-reflectron, and in particular permits analysis of material forming ions with m values of several thousand atomic mass units. A mass spectrum is given for the trimer rhenium bromide $(ReBr_3)_3$ with m up to 1300 amu, obtained by means of an experimental mass-reflectron; the resolution in the peak width at half-height is up to 3500. Advantages of the mass-reflectron over the ordinary time-of-flight mass spectrometer are discussed.

INTRODUCTION

It is well known that nonmagnetic time-of-flight mass spectrometers (TFS)[1-7] have a number of advantages over other types of mass spectrometers. Among the advantages are: 1) the possibility of recording a mass spectrum in a few microseconds, 2) the unlimited mass range for the ions studied, and 3) the possibility of panoramic display of both the entire mass spectrum and any individual parts of it.

The main deficiency of TFS has until recently been their poor resolution, which cannot be made greater than several hundred for apparatus parameters acceptable in practice. It has not been possible to overcome this limitation by improvements of the ordinary TFS arrangement during the course of about 20 years.

The principal physical factor which limits the resolution is the existence of a spread in the initial velocities of ions produced in a single equipotential plane of the source. In the case of anomalously large spread of initial ion energies (tens and hundreds of electron volts as occurs, for example, in laser or spark sources), the usual TFS does not provide the possibility of obtaining a resolution which is of practical interest. The velocity filters which can be used in such mass spectrometers, although they increase the resolution, substantially reduce the sensitivity.

The mass-reflectron is a new type of nonmagnetic time-of-flight mass spectrometer with focusing of the time-of-flight of the ion packets on the basis of energy[8-10]; all of the advantages of nonmagnetic TFS are combined with high resolution in this spectrometer.

PRINCIPLE OF OPERATION OF THE DEVICE

In the usual type of TFS, space-time focusing of the ions packets is accomplished at the end of a field-free region (in the detector plane)[1-5]. It is easy to show that the thickness (Δl) of packets arriving at the detector is determined almost completely by the initial energy spread of the ions ($q\Delta U$),

$$\Delta l \approx L\sqrt{\Delta U / U}, \tag{1}$$

where qU is the ion energy in the drift space and L is the drift length (the focal length of the source). In contrast to the usual TFS, the mass-reflectron accomplishes space-time focusing of the ion packets near the source at a distance L' ($L' \ll L$). Since the packet thickness in the plane of the space-time focusing is proportional to the focal length, then, other things being equal, Δl in the mass-reflectron is appreciably smaller than in ordinary TFS. An ion packet with a given ratio m/q focused near the source contains ions with a set of energies from U_{min} to U_{max}, due mainly to the difference in the paths traversed by the ions in the field of the extracting pulse. In moving through the field-free space the packet expands as the result of the difference in ion velocities, the time of motion of the ions in the drift space being $T_d \sim 1/\sqrt{U}$. To focus the ion packets in the detector plane it is necessary that the time of motion in the apparatus of ions with a given m/q ratio be identical. In order to satisfy this condition, at the end of the first portion of the drift space is placed a reflecting system in the form of a uniform electrostatic field in which the time of motion of the ions is $T_0 \sim \sqrt{U}$. With an appropriate choice of the parameters of the reflecting system, the time of movement of ions from the source to the detector can be made practically independent of their energy, and packets with a thickness close to the initial thickness of the packets in the space-time focusing plane can be obtained at the detector plane.

Thus, while the resolution in an ordinary TFS cannot be increased by a simple increase in the drift length, since in this case the time of flight and the packet thickness in the detector plane also increase, on the other hand in the mass-reflectron the resolution increases in proportion to the length of the drift space.

In order to accomplish second-order focusing of the time of flight of the ions on the basis of energy, an additional gap with a retarding electric field is necessary in front of the reflecting system[8-10].

A diagram of a mass-reflectron with second-order focusing of the time of flight is shown in Fig. 1. Ions produced in the source I are extracted into the drift space L_1 in a direction parallel to the axis of the device. Passing through the deflecting plates DP, the ions change their path direction by an angle α. After passing through the reflecting system RS the ions enter the second part of the drift space L_2, at the end of which an electron multiplier is located.

In order to achieve space-time focusing near the source, it is necessary to reduce the ratio $p = E_2/E_1$ in comparison with the ordinary TFS, where $E_1 = U_1/d_1$ is the electric-field strength produced by an extracing pulse of magnitude U_1 in the first gap of the source of width d_1, and $E_2 = U_2/d_2$ is the field strength produced by the ac-

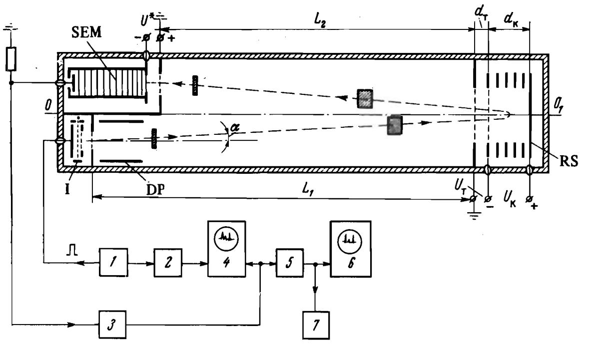

FIG. 1. Diagram of the mass-reflectron. I–Ion source, DP–deflecting plates, RS–reflecting system, SEM–electron multiplier, 1–rectangular pulse generator, 2–delay line, 3–wideband amplifier, 4–wideband oscillograph, 5–stroboscopic attachment, 6–low-frequency oscillograph, 7–electronic potentiometer.

celerating potential difference U_2 in the second gap of the source of width d_2.[9]

For focusing of ion packets in the plane of the detector, the reflecting-system parameters must satisfy the following relations[9-10]:

$$U_T \approx 0.7U_0, \quad U_K \approx 0.45U_0, \quad d_T \approx 0.008L, \quad d_K \approx 0.06L, \tag{2}$$

where $qU_0 = q(U_{\text{min}} + U_{\text{max}})/2$ is the average energy of the ions in the drift space, and U_T, d_T, U_K, and d_K are the potential differences and interelectrode distances respectively in the retarding and reflecting gaps. The drift length L can be arbitrarily distributed between the legs L_1 and L_2.

RESOLUTION AND SENSITIVITY OF THE MASS-REFLECTRON

The resolution of the mass-reflectron in peak width at half-height can be calculated from the formula

$$R_{50\%} = L^* / \Delta l^*, \tag{3}$$

where L* is the total effective drift length and Δl^* is the total effective packet thickness in the detector plane.

It is easy to show that the ion motion time in the reflecting system is equivalent to the time required for traversal of some portion of the drift space L_3^* whose length can be calculated from the formula

$$L_3^* \approx 4d_K \frac{U - U_T}{U_K}. \tag{4}$$

Thus,

$$L^* = L_1 + L_2 + L_3^*. \tag{5}$$

The total effective packet thickness at the detector entrance can be calculated from the formula

$$\Delta l = \Delta l_1 + \Delta l_2 + \Delta l_3 + \Delta l_4, \tag{6}$$

where Δl_1 is the packet thickness in the plane of space-time focusing near the source, Δl_2 is the packet expansion due to the action of the reflecting system, Δl_3 is the packet expansion due to deviation of its plane from a location perpendicular to the axis of the apparatus, and Δl_4 is the effective depth of the detector entrance. The quantity Δl is practically completely determined by the spread in initial ion energies (see Eq. (1), where L = L′ is the effective drift length to the plane of space-time focusing).

The packet broadening due to inaccuracy of space-time focusing amounts to a fraction of a per cent of the total packet thickness and can be neglected. For optimal adjustment of the reflecting system, it also produces practically no broadening of the packet ($\Delta l_2 \approx 0$[10]).

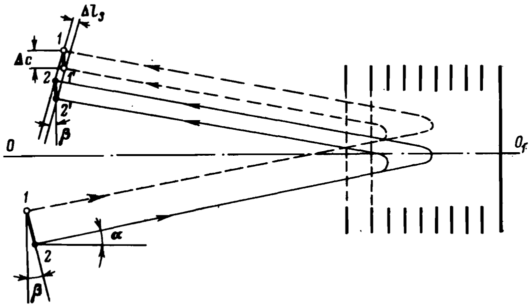

FIG. 2. Expansion of ion packet as the result of deviation of its plane from the position perpendicular to the device axis. 1-2–Ion packet plane at beginning of drift, 1-1′ and 2-2′–planes in which ions from points 1 and 2 of the initial packet appear as the result of ion energy spread.

The value of Δl_3 can be obtained as follows. If the plane of a packet leaving the source 1–2 is not perpendicular to the device axis (see Fig. 2), then at the end of the drift space each point of the initial packet, containing ions of all energies from U_{min} to U_{max} moving at an angle α, is converted to a packet of width Δc perpendicular to the 00_1 axis:

$$\Delta c \approx 4\frac{d_K}{U_K}(\sqrt{U_{max} - U_T} - \sqrt{U_{min} - U_T})\,\text{tg}\,\alpha. \tag{7}$$

The least packet thickness in this case is

$$\Delta l_3 = \Delta c \sin \beta. \tag{8}$$

In order to obtain the minimal value of Δl_3, it is necessary that the angle β be zero, which is achieved by appropriate location of the source. Deflection of the ion trajectory by an angle α is accomplished by means of deflecting plates which, while changing the direction of motion, do not change the orientation of the plane of the packet in space. Distortions introduced by the deflecting plates are insignificant, since the distance between the plates is more than a factor of two greater than the beam diameter and the plates are rather long.

If a secondary-emission multiplier is used to detect the ions, the ions at the end of the drift space must be accelerated to reduce the effective thickness of its entrance. For this purpose an accelerating gap with a potential difference U* is placed in front of the multiplier. Then

$$\Delta l_4 = l_{\text{mul.}}\sqrt{U_0 / (U_0 + U^*)}, \tag{9}$$

where $l_{\text{mul.}}$ is the geometrical depth of the first dynode.

It was found that the expansion of packets due to repulsion of the ions by space charge and the nonideal properties of the fields in the plane of the gridded electrodes is negligible.

When we take into account all of the above, we can write down an expression determining the resolution of the mass-reflectron in the following form:

$$R_{50\%} \approx \left(L_1 + L_2 + 4d_K \frac{U - U_T}{U_K}\right)\left(L'\sqrt{\frac{\Delta U}{U}} + l_{\text{mul.}}\sqrt{\frac{U_0}{U_0 + U^*}}\right)^{-1}. \tag{10}$$

In loss of ions the mass-reflectron differs little from ordinary TFS with drift lengths equal to the effective drift length of the mass-reflectron. Additional losses of ions occur only as the result of their traversal of the grids of the reflecting system in the forward and reverse directions.

From consideration of the arrangement of the mass-reflectron it follows that it has the following features: 1) the resolution of the mass-reflectron increases in proportion to the ion drift length, and for a given drift length can be made substantially greater than in ordinary TFS; 2) with an anomalously large spread in initial energies, the sensitivity of the mass-reflectron can be made substantially greater than the sensitivity of ordinary TFS; 3) the effective drift length of the mass-reflectron can be made substantially greater than the overall length of the apparatus; 4) less power supply voltage is required for the mass-reflectron source, which reduces the requirements for electronics.

STUDY OF AN EXPERIMENTAL DEVICE

An experimental sample of the mass-reflectron had the following design parameters:

$$L_1 = 820\,\text{mm}, L_2 = 780\,\text{mm}, d_T = 5 - 10\,\text{mm},\ d_K = 100\,\text{mm},$$
$$U_2 = 600 - 1500\,\text{V},\ U_T = 400 - 1200\,\text{V},\ U_K = 300 - 700\,\text{V},\ \alpha = 2°.$$

Guard rings were used to produce a uniform field in the reflecting system. The ion-source design is similar to that used in ordinary TFS. Ionization is produced by electron impact; the electron energy can be varied over the range 10–200 eV. A uniform magnetic field of intensity of the order of 200 Oe was used for focusing the electron beam. The electron collector current could be controlled over the range 100 μA–5 mA. The ion extraction pulse has a height of 300 V, a duration of 2×10^{-6} sec, and a repetition frequency 1–10 kHz. The electron gun could operate both continuously and with the electron beam turned off during extraction of the ions. It was also possible to delay the ion-extraction pulses relative to the pulses cutting off the electron beam. The openings in the electrodes of the source and reflecting system are covered with fine grids with a mesh size of $50 \times 50\ \mu$ and a transparency of about 80%.

A standard Venetian-blind electron multiplier (type VEU-1A) with a gain of the order of 10^5 was used in the apparatus. The first dynode was replaced by a specially prepared dynode with a geometrical depth of the order 0.3 mm. The design of the first dynode prevented direct incidence of ions on the second dynode. In front of the multiplier was placed an accelerating gap with plane gridded electrodes.

The signal from the multiplier output was amplified by a wideband transistorized amplifier with a gain K = 300 and a bandwidth f = 180 MHz. The spectrum was recorded either on the screen of a wideband oscillograph or by a stroboscopic system[11] on the screen of a low-frequency oscillograph or electronic potentiometer chart.

The resolution of the mass-reflectron was calculated for these parameters, taking into account the actual multiplier and the amplifier-circuit bandwidth. It was found to be in the range

$$R_{50\%} = 2400 - 3500$$

depending on the specific conditions used, for ions with a ratio $m/q \geq 200$. The mass spectrograms shown indicate the good agreement of the theoretical and experimental values.

The mass-reflectron was used to obtain the spectra of a number of materials and also the lines of the residual spectrum in the heavy-mass region. In a number of cases resolved mass multiplets were obtained for the first time by means of non-magnetic TFS. The most interesting illustrations of the operation of the mass-reflectron are photographs of the spectra obtained from the wideband oscillograph screen, since in this case one of the most important advantages of TFS is realized—its fast action. Figure 3a shows the mass spectrum of mercuric iodide HgI_2, and Fig. 3b two neighboring lines of this spectrum $(^{199}Hg^{127}I_2)^+$ and $(^{200}Hg^{127}I_2)^+$ with respective masses of 453 and 454. The resolution at half-height of the peaks is $R_{50\%}$ = 2800. More intense lines of I^+ and

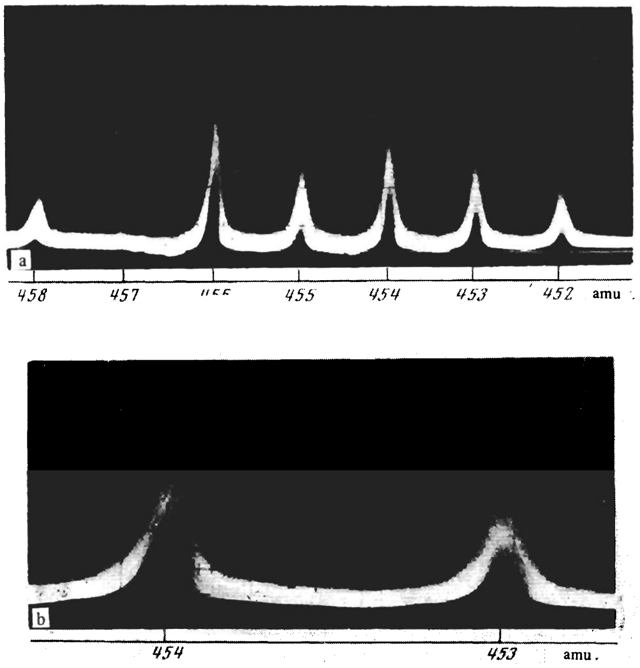

FIG. 3. a–Oscillogram of a portion of the mass spectrum of mercuric iodide HgI_2; b–oscillogram of two neighboring mass lines of mercuric iodide $(^{200}Hg^{127}I_2)^+$ and $(^{199}Hg^{127}I_2)^+$ with respective masses of 454 and 453 amu.

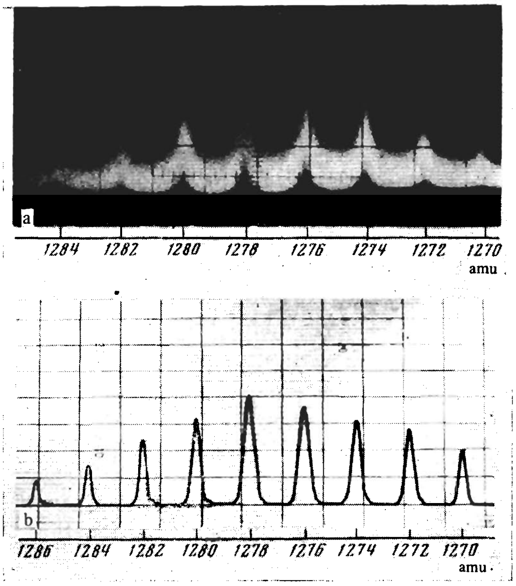

FIG. 4. Oscillogram of part of the mass spectrum of rhenium bromide: a–group of lines corresponding to the trimer of rhenium bromide; b–group of lines corresponding to the trimer of rhenium bromide recorded by the stroboscopic system.

Hg^+ and also less intense lines of Hg^{++} and HgI^+ were observed at the same time in the mass spectrum.

Figure 4 shows the mass spectrum of rhenium bromide evaporated in the form of the monomer $ReBr_3$, the dimer $(ReBr_3)_2$ and the trimer $(ReBr_3)_3$. Ions of the general formula Re_nBr_m were observed in the spectrum, where $n = 0-3$, $m = 0-9$, and also ion groups with the general formula $Re_nBr_mO_k$.[12,13] Figure 4a shows the mass spectrum of the trimer $(ReBr_3)_3$ with ion masses in the range 1266—1290 amu, and Fig. 4b the mass spectrum of the trimer obtained by means of a stroboscopic system. The resolution is $R_{50\%} \geq 3000$.

The most objective evaluation of the sensitivity of the ion-optical system of a TFS, it appears to us, is the minimal partial pressure of one gas isotope for which packets containing on the average one ion in each sweep of the spectrum are observed in the mass spectrum.

A sensitivity figure[7] often used in description of equipment characterizes the apparatus as a whole, including the stroboscopic system, and so forth, and corresponds to a substantially increased time constant of the system. Although this sensitivity figure has a practical importance, particularly in advertising, it does not represent the sensitivity of the ion-optical part proper of the mass spectrometer.

Comparing the mass-reflectron with ordinary TFS and taking into account the effective drift length, we found that the sensitivity is practically identical with that of ordinary TFS. In the mass-reflectron one ion per packet reaches the detector for a partial pressure of argon of $\sim 5 \times 10^{-9}$ mm Hg.

CONCLUSION

1. The actual construction of a mass-reflectron does not involve especial difficulties in comparison with the ordinary TFS. The mass-reflectron is stable in operation, and its design permits its resolution and sensitivity to be changed easily.

2. The investigations carried out have shown that the resolution achieved of 3500 at the half-height of the peak is not a limiting value, and means of further improvement are apparent.

The authors express their sincere gratitude to Professor N. I. Ionov for helpful discussions and for his constant interest in this work.

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Translated by C. S. Robinson
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