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Full Length Article

High performance gridless ion mirrors for multi-reflection time-of-flight and electrostatic trap mass analyzers

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ABSTRACT

The paper summarizes original developments of gridless ion mirrors for high-resolution multi-reflection time-of-flight mass spectrometers (MR TOF MS). Optimized mirror geometries and electrostatic field distributions reach up to the 5th order isochronicity with respect to the energy spread and up to the 3rd order full isochronicity per energy, spatial and angular spreads of ion packets. Using a retarding focusing field at the mirror entrance doubles the ion transport energy at limited highest voltages. In planar analyzers with a zig-zag ion path, quasi-planar mirrors eliminate the 2nd order dependence of the flight time on the ion packet width in the drift direction. Improved MR TOF analyzers of 1 m size provide well over one million aberration limit at realistic ion packets parameters past orthogonal accelerators. Because of high order isochronicity the aberration limit rapidly grows with the analyzer size or when using narrower ion packets. In experiments, improved analyzers with one meter size demonstrate up to 300 000 mass resolving power at the full mass range and 500 000 at the restricted mass range. Improved ion mirrors with two-dimensional electrostatic fields are applicable for TOF MS, electrostatic traps and open electrostatic traps in planar and hollow cylindrical geometries.

1. Introduction

In 1956 Alikhanov [1] proposed reflecting ions in electrostatic fields to reduce the time per energy spread. Mamyrin [2] implemented a two-stage ion mirror in a time-of-flight (TOF) analyzer and demonstrated yet another advantages of ion mirrors – folding ion trajectories for a longer flight path and using strong ion accelerating fields for reducing the so-called "turn-around time" in ion sources. Since then an electrostatic ion mirror became a key ion-optical element in TOF mass spectrometers (MS). Mamyrin's dual stage ion mirror with grid covered electrodes still remains very popular in commercially produced TOF MS. Grids have to be extremely fine to minimize the angular ion scattering and geometrical ion losses, which poses technological challenge in singly reflecting TOF MS and prevents their use in further described multi-reflecting time-of-flight (MR TOF) mass analyzers.

To overcome grid limitations, multiple attempts were made to design gridless ion mirrors. First gridless mirrors were intended for one-stage reflectron TOF MS and mostly tried to copy the field structure of a standard reflectron mirror [3–5]. After an MR TOF MS with multiple gridless mirrors was proposed by Wollnik [6], several ion mirror designs for such spectrometers have been developed [7–9]. However, up to a certain point gridless mirrors provided a limited set of ion-optical properties: a geometric focusing and the first order TOF focusing with respect to the ion energy spread. In alternative parabolic ion mirrors [10–13] with the quadratic distribution of the electrostatic potential the perfect time per energy focusing is negated by a spatial ion defocusing and a small spatial acceptance of ion mirrors.

The ion-optical quality of gridless ion mirrors has been substantially improved in 2004 [14,15]. Authors proposed, simulated, and experimentally tested a high performance gridless planar ion mirror controlled by four electrode voltages. The mirror provides for the third-order TOF focusing with respect to the ion energy spread and for the overall and complete second-order TOF focusing with respect to the spatial, angular and energy ion spreads, which resulted in the energy acceptance of 6% and the spatial acceptance of 6 mm × 15 mrad at 30 mm mirror window height. The mirror has been developed for reaching the mass resolving power of R = 100 000 at the full mass range and for R = 200 000 at

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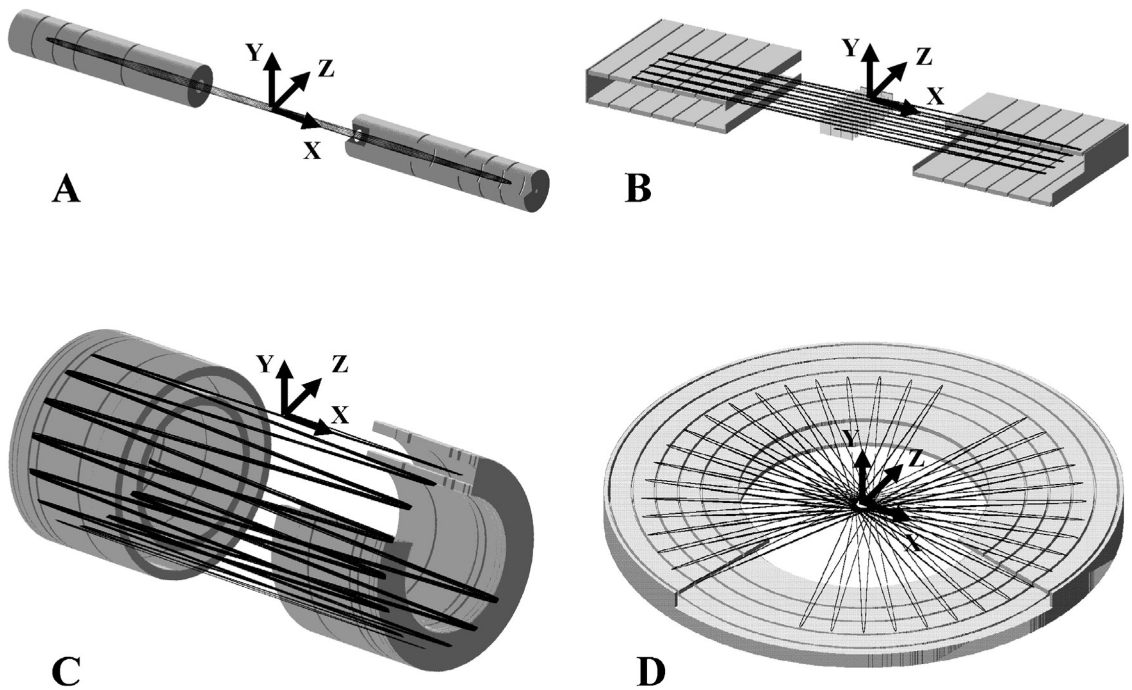

Fig. 1. Ion motion in MR TOF mass analyzers with different types of ion mirrors: (A) axially symmetric, (B) planar, (C) hollow cylindrical, and (D) pancake ones. In all drawings parts of the mirrors are cut out to show electrode sections. In case (B) an array of periodic 2D lenses, refocusing ions in the Z-direction, is shown between the mirrors.

a restricted mass range [16]. An axially-symmetric ion mirror with similar ion-optical design was also implemented into the shuttle-type MR TOF MS at JLU Giessen [17,18]. For $^{133}Cs^{+}$ ions after a flight time of 49 ms the latter MR TOF MS experimentally achieved 600 000 mass resolving power.

The present paper summarizes further original developments and improvements of high performance gridless ion mirrors for MR TOF MS. Further improved ion optical quality allows increasing the energy and spatial acceptance of the MR TOF mass analyzers, thus increasing their mass resolving power and/or sensitivity per analyzer size. In particular, a range of ion mirrors with the full third order isochronicity and up to the fifth order time per energy focusing has been proposed in Refs. [19,20]. The ion-optical quality of such mirrors has been verified in experimental tests, demonstrating the mass resolving power of 300 000 at the full mass range and up to 500 000 at a restricted mass range [21]. Ion mirrors discussed in the paper may be applied to a variety of isochronous electrostatic analyzers, such as time-of-flight mass spectrometers, open trap and electrostatic trap mass-spectrometers [21,22], constructed in a variety of topologies, corresponding to planar, coaxial, and hollow cylindrical ion mirrors.

2. Geometry types of gridless ion mirrors

Historically first gridless ion mirrors [3,7] were designed as axially symmetric ones built of coaxial rings or round aperture electrodes. Two opposed coaxial mirrors are separated by a drift space to form an isochronous shuttle-type electrostatic trap for axial ion oscillations in the *X*-direction, as shown in Fig. 1A. Ions are pulsed injected and pulsed ejected through apertures in the cap electrodes [9,18,23]. Typically, both mirrors are identical, though different mirror geometries can be used [9]. Axially symmetric TOF mass analyzers have an advantage of providing equal spatial and TOF focusing properties in both transverse directions *Y* and *Z*. The main drawback is a closed ion motion cycle, so that only a narrow mass range can be accepted onto a TOF detector in order to prevent spectral confusion.

Planar ion mirrors [8,16] may be built of flat electrodes elongated in one (*Z*) direction, thus forming a two-dimensional 2D field in the *XY* plane with zero field in the *Z*-direction at sufficient distance from the mirror *Z*-boundaries, typically exceeding a couple of calibers. Planar ion mirrors allow organizing a periodic zig-zag ion motion by reflecting ions between mirrors in the *X*-direction and spatially focusing ions in the *Y*-direction while drifting ions in the *Z*-direction. In this case, ion trajectories are not closed into cycles, allowing non-interfering ion injection and ion detection, necessary for the mass analysis in the full mass range. Since planar mirrors do not possess any focusing properties in the drift *Z*-direction, achieving long ion flight paths with several tens of reflections requires using additional focusing means in the drift direction, such as 2D periodic lenses [24–26] as shown in Fig. 1B.

A further variety of ion mirror geometries can be found in Ref. [22]. In particular, one can bend a planar mirror in the *Z*-direction this way closing it into a so-called hollow cylindrical mirror. To retain the ion optical quality, the curvature radius shall be much larger than the *Y*-width of the electrode window. Such a mirror provides much denser folding of ion trajectory per analyzer volume and eliminates boundary fields at the mirror *Z*-edges. The curvature of the electrostatic field equipotential lines in the Z-direction creates a force moving ions towards the center, so that ions, injected into the analyzer at small inclination angle to the *X*-axis, approximately follow a "mean" cylindrical surface between the mirror electrodes and thus perform a cylindrical zig-zag motion as shown in Fig. 1C.

Alternatively, the planar mirror electrodes can be bent in the X-direction with a curvature radius much larger than the *Y*-width of the electrode window, forming a pancake mirror design rotationally symmetric about the *Y*-axis. If ions are injected into the pancake analyzer in the *XZ*-plane and miss the rotational symmetry axis, they form oscillating trajectories not closed into cycles as shown in Fig. 1D. A central lens [27] plays the role of periodic lens developed for planar analyzers.

It is important to emphasize that the electrode sections and geometrical focusing properties in the *XY*-plane as well as TOF focusing properties of all above referred ion mirrors are very similar, so that