

# A Segmented Time-of-Flight Mass Spectrometer

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**Abstract,** The present paper describes the design of a time-of-flight mass spectrometer (TOFMS) in which the single flight tube of a conventional TOFMS has been replaced by several cylindrical electrostatic lenses in tandem. By a judicious choice of voltages on these lenses an improved TOFMS has been realized which has a superior mass and energy resolution, shorter flight lengths, excellent signal-to-noise ratio, and less stringent requirements on the bias voltages.

## **1. Introduction**

Time-of-flight mass spectrometers [1] are commonly used in laboratory research related to particle and photon impact ionization and dissociation of molecules and clusters. They are mainly employed for the measurement of intensities of various ionic species and their kinetic energies. For achieving a high mass and energy resolution these instruments generally comprise long flight tubes. This necessitates high ion extraction voltages [2] and clean environment. We have developed an instrument which is based on the design principles of a TOFMS. However, instead of utilizing a conventional long and continuous flight tube we have used several cylindrical electrostatic lenses in tandem, By applying proper voltages on the various lenses the ions are confined to travel very close to their axes. This results in a superior mass and energy resolution, shorter flight lengths, excellent signal to noise ratio, and less stringent requirements on various bias voltages than the conventional TOFMS.

## **2. Apparatus and theory**

A schematic diagram of the present TOFMS along with various electronic devices is shown in Fig. 1. For the experimental data presented here ions were generated by an energy selected electron beam which collided with the target molecular beam at  $90^\circ$ . They were then extracted out of the collision region at  $90^\circ$  to both beams by a pair of molybdenum wire meshes and the extracted ions were directed towards the set of lenses for mass and energy analysis. A pulsed ion extraction method was employed [3]. For this purpose the electron beam was pulsed with a pulse width of about 100 ns. Right after the collision of this pulsed

electron beam with the target molecules an electrical pulse (of about 2 micro-second width and of 50V amplitude) was applied to the extraction grids. The extracted ions passed through an electron filter which had a weak magnetic field (-25 to 50 Gauss) in a direction perpendicular to the trajectories of ions. This magnitude of the field was sufficient to remove electrons but did not effect the ion signal. The time of flight of each ion was measured by utilizing the conventional delayed coincidence technique [4]. This time of flight is related to the mass and the initial kinetic energy of the ion through eqs. (1) and (3), respectively.

The novelty of the present instrument lies in the fact that the flight tube is broken up into several cylinders each of which is given a different voltage so that the ions can be confined very close to the axes of the cylinders during their flight through them. In the following, we will examine the effect this arrangement has on the relationship between the mass of the ion and its time of flight. For the situation where one single flight tube is employed the time of flight  $T$ , the mass  $m$  of the ion of charge  $q$ , the length  $L$  of the flight tube, and the voltage  $V$  on it are related to each other through the following relation:

$$\begin{aligned} T &= L (m/2Vq)^{1/2}, \\ &= K (m/q)^{1/2}. \end{aligned} \tag{1}$$

If the flight tube is broken up into several cylindrical elements, say four, of lengths  $L_1$ ,  $L_2$ ,  $L_3$ , and  $L_4$  with corresponding voltages  $V_1$ ,  $V_2$ ,  $V_3$ , and  $V_4$ , respectively, then (neglecting fringe fields between the cylinders) eq. (1) can be written in the following form:

$$\begin{aligned}
T &= L_1(m/2qV_1)^{1/2} + L_2(m/2qV_2)^{1/2} + L_3(m/2qV_3)^{1/2} + L_4(m/2qV_4)^{1/2}, \\
&= K_1(m/q)^{1/2}.
\end{aligned}
\tag{2}$$

Thus, from eq. (2) it is clear that the proportionality of T to  $(m)^{1/2}$  is still maintained except for the calibration constant  $K_1$  which is different. Its value can be obtained by measuring the flight times of rare gas atoms.

The kinetic energy E of an ion is related to its TOF through the following relation:

$$E = (1/2) m (L^2/T^2), \tag{3}$$

where L is the length of the flight path. By differentiating the above equation one can easily obtain the following two relations:

$$\Delta E/E = -2. \Delta T/T, \tag{4}$$

$$\Delta m/m = 2. \Delta T/T. \tag{5}$$

From these equations it is clear that mass and energy resolutions of the instrument depend on the time resolution of the instrument. In an ideal case for monoenergetic ions, where trajectories of all ions are **parallel** to the axis of the flight tube, AT is limited only by the smallest time which the electronic timing devices of the instrument can measure. However, in practical situations ions do not follow ideal trajectories. They are generally curved and, therefore, there is a spread in arrival times of ions of either same energies but different masses, or same masses but different energies. According to our calculations, performed by plotting the trajectories of various ions for the present TOFMS, we find that AT should be of the order of 0.016 ms for Nitrogen ions, This translates to a mass resolution of 0.041 amu. Similarly, the energy resolution for 5 eV Nitrogen ions corresponds to about 0.015 eV. However, in a practical situation these limits are never reached due to various limiting factors. We find that the present instrument can easily resolve 1 amu for ions of about 18 amu which corresponds to an energy resolution of about 0.278 eV.

The trajectories of ions through the present system of electrostatic cylindrical lenses were calculated by utilizing SIMION program [5]. Two different cases were considered. In the **first** case, the voltages on the various elements were chosen in such a way that a high mass resolution ( $\Delta m \sim 1$  amu) was achieved for *ions* with thermal energies. In the second case, the voltages were chosen in such a way that ions of mass  $m$  but of different kinetic energies (ranging from thermal to 15 eV) were separated. It was concluded from these calculations that by judiciously choosing the voltages on the various lens elements either high mass resolution or high energy resolution could be obtained.

### 3. Results

The present instrument has been extensively used in our laboratory over a period of past two years for generating mass spectra of both positive and negative ions resulting from

the electron impact ionization and dissociative attachment of molecules. Figure 2 shows the mass spectrum for 70 eV electron impact ionization of the background gases present in the vacuum chamber at a pressure of about  $1 \times 10^{-7}$  Torr. It is clear that a unit mass resolution is achieved and the signal to noise ratio is excellent. Figure 3 presents positive ion spectra resulting from ionization and dissociative ionization of CO<sub>2</sub> and N<sub>2</sub>. This figure is self explanatory and shows that the instrument has performed well for analyzing the kinetic energies of various energetic ions born as a result of electron impact dissociation of parent molecules.

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## References

- [1]. Price D and Milnes G J, 1990, The renaissance of time-of-flight mass spectrometry  
Int. J. Mass Spectrom. Ion Processes 99, 1-39
- [2]. Wiley WC and McLaren IH, 1955, Time-of-Flight mass spectrometer with improved resolution Rev. Sci. Instrum. 26, 1150-7.
- [3]. Krishnakumar E and Srivastava SK, 1990, Cross sections for the Production of  $N_2^+$ ,  $N^+ + N_2^{2+}$  and  $N^{2+}$  by Electron Impact, J. Phys. B: At. Mol. Opt. Phys. 23, 1893-1903.
- [4] Bell RE, 1966, Alpha, beta and gamma ray spectroscopy, ed. K. Siegbahn, (Amsterdam: North-Holland) 2,911-6.
- [5] S] MION, EGG-cs-7233 Rev. 2 prepared by EG&G Idaho Inc., P. O. Box 1625, Idaho Falls, ID 83415, USA.

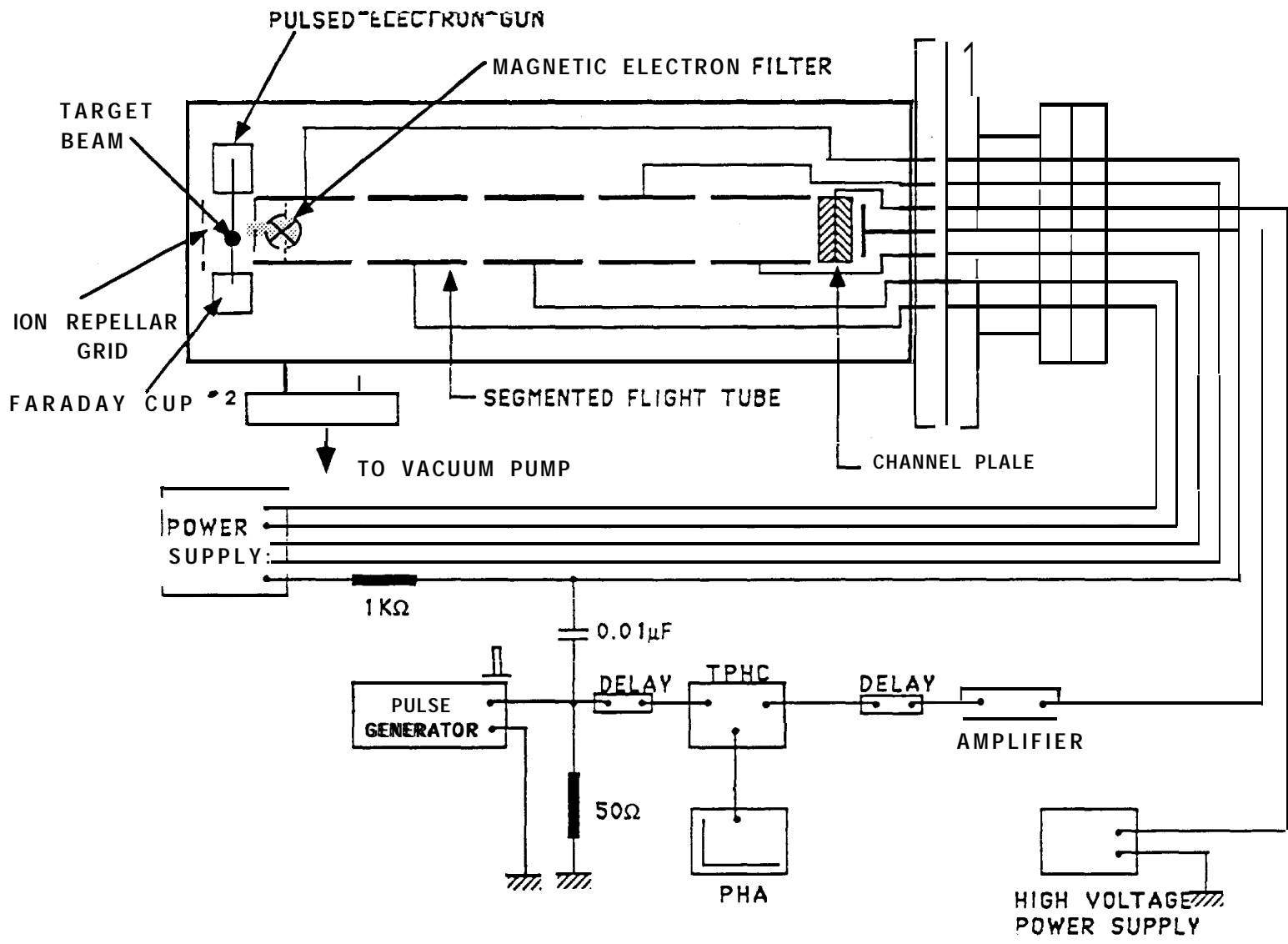


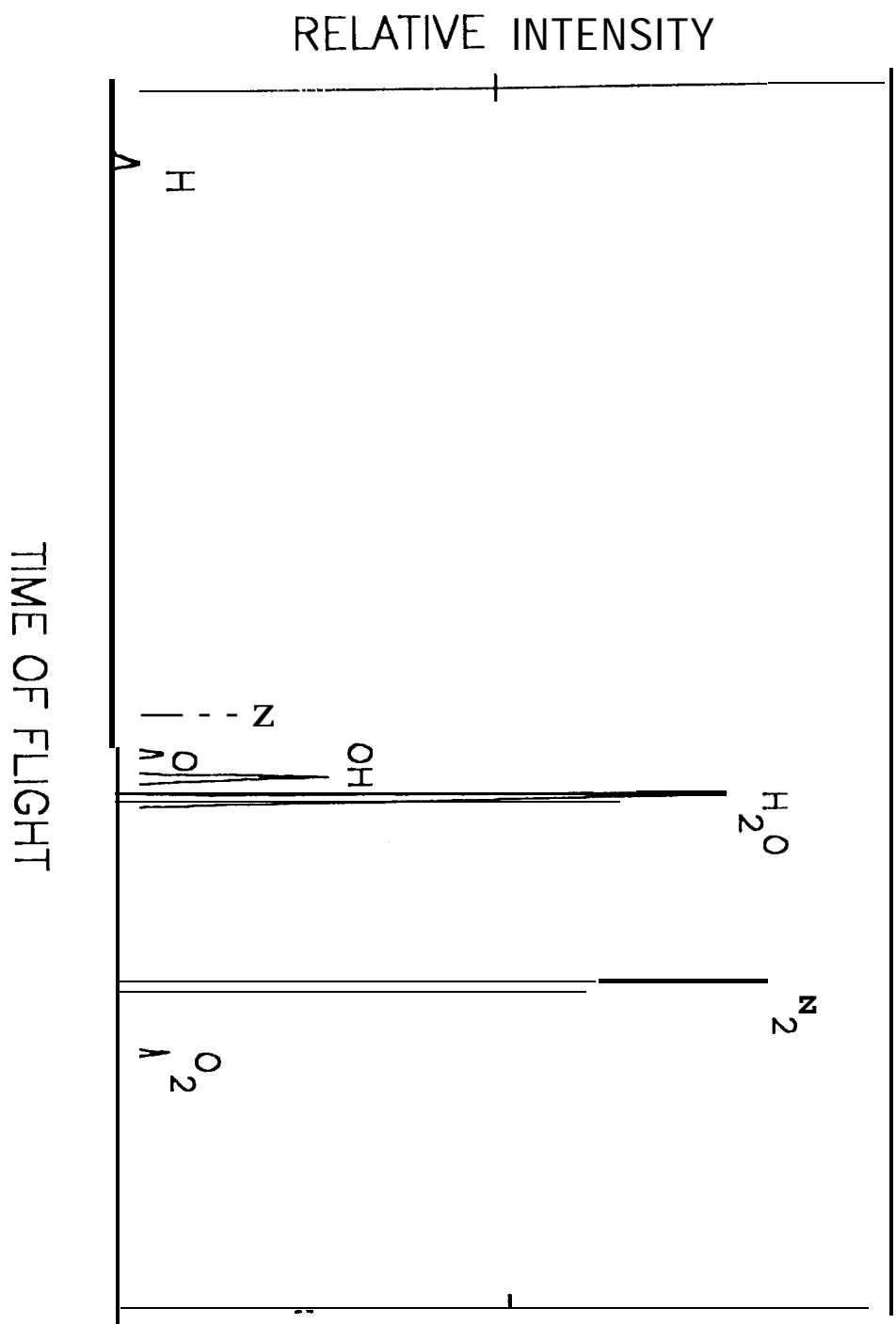
**Figure captions**

Figure 1. Schematic diagram of the TOFMS.

Figure 2. Mass spectrum of the residual gases in the vacuum chamber at a background pressure of about  $1 \times 10^{-7}$  Torr.

Figure 3. Ionization and dissociative ionization spectra of CO<sub>2</sub> and N<sub>2</sub>, respectively. They show the kinetic energy distribution of energetic ions.





Relative Intensity

