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IMPROVED MASS RESOLUTION.

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Abstract :

An electrostatic mirror has been built to achieve time focussing and high mass resolution with a new ^{252}Cf time of flight mass spectrometer. The first results show that $\frac{M}{\Delta M(50\%)}$ values are around 2500 for organic molecules. The apparatus is described and results are presented. Future applications for metastable ion studies are briefly discussed.

It has been shown many years ago (1) (2) that relatively high mass resolution could be achieved with time of flight mass spectrometer for inorganic molecules like mercury iodide and rhenium bromide. The principle of an ion electrostatic mirror acting as a time focussing method was experimentally developed by these authors. Since that time, little attention was paid to time focussing time of flight (T.O.F.) mass spectrometers for heavy organic molecules although new ionisation-desorption techniques (3-6) associated, or not, with normal T.O.F. mass spectrometer have greatly contributed to the field of mass spectrometry (7-13). High mass resolution for light organic molecules (< 100 ua) have however already been obtained with a reflex time of flight mass spectrometer and a pulsed laser ionization source (14).

During the past recent years, very fast timing electronic device have became available as a result of technical and fundamental researches mainly originating from nuclear physic laboratories. Accurate T.O.F. measurements are routinely made in nuclear physic experiments either for M.e.V. ion beam velocity measurements (15-16) or for identifying in flight new exotic nuclei (17-19). Others new analytical methods like "Rutherford back scattering" (20) or "elastic recoil analysis" (21) based on precise T.O.F. have also emerged recently.

In this short paper we present the first results obtained with a time focussing ^{252}Cf T.O.F. mass spectrometer built in our Institute. It is shown that the mass resolution at half maximum of the T.O.F. peaks is around 2.500 for heavy organic molecules ($\sim$1000 ua). The same mass spectrometer (M.S.) allows to measure simultaneously with charge species, the neutrals resulting from a fragmentation in flight in the field free space region. Coincidence measurements can therefore be performed for metastable ion studies.

I. EXPERIMENTAL

A standard ^{252}Cf M.S. has been slightly modified as shown in fig. 1.
The ion reflecting part ————————————is composed of two retarding
potential region. The first one is composed of two thin and parallel grids
(5 mm apart) at potentiel $U_{G_1} = U_{G_0} = 0$ and $U_{G_2} = \frac{2}{3} U_{G_3}$. The second part is
composed of 6 equidistant annular electrodes with fixed potential
$E_i \underset{(i=1\grave{a}6)}{=} i \frac{(U_{G_3} - U_{G_2})}{6}$ and a third grid fixed at the potential U_{G_3} ($\pm$ 8 or
$\pm$ 10 KV in the present experiment). Beyond this third grid a set of normal
channel plates (channel electron multiplier array) is used to detect neutrals
but can also be used to detect ions in direct T.O.F. measurements (i.e. with
no reflexion).

After having been desorbed and accelerated the molecular ions enter
the field free region and $\overset{pass}{\sqrt{}}$ through annular channel plate detectors before rea-
ching the first grid of the mirror. Then ions with different initial velocities
are reflected at different points in the second retarding electric field region.
On the return trajectories, time differences are partially compensated when they
are detected by the specially built annular detectors.

Conventional fast electronic equipment has been used as shown in the
electronic diagram in fig. 1. The multistop time digital converter (0.5 nsec/
channel) was built at the Institute (22) as well as the constant fraction discri-
minators (23). One recalls that measurements are made event by event with random
start signals (400/sec) given by fission fragments from a ^{252}Cf source. For each
start signal the entire time scale is explored (64 or 128 μsec). The total
pure electronic time resolution was measured to be less than 60 picoseconds. Howe-
ver, since fission fragments have a natural mass and energy distribution a time
spread is therefore introduced in the secondary ion T.O.F. measurement. This time
spread has been measured and fig. 2 shows a time of flight spectrum which repre-
sents T.O.F. differences between heavy and light fragments emitted at 180° and
hitting either the electron converter foil on one side or the molecular deposit
on the other side. The width of this time distribution ($\sim$ 3 nsec) could be reduced

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by choosing carefully another geometrical arrangement.

In the results shown in the next section, this initial time width contribute for 3 nsec at half maximum in the secondary ion T.O.F. peaks. As this
must be added quadratically with other effects this broadening effect contributes for only
10 % of the total width (at mass 747).

We will not derived here all the relations which have led to define the construction parameters of the reflecting system. Detailed calculation on the principle can be found in ref. (1) and (2) as well as in ref. (24) for the present apparatus. Let us just recall the basic equations and the conditions which must be satisfied to achieve a good time focussing. Distances and grid potential parameters are defined in fig. 1. We have $U_o = U_s - U_{G_o}$,
$\cdot \cdot = U_1 + e_o$ and $U_2 = U_{G_2} - U_{G_1}$, $U_S = U_{G_3} - 50$ volts
e_o is the initial ion kinetic energy. With the following relations :

$$A = \frac{L + L'}{4d_3} \cdot \frac{U_3}{U_o}$$

$$n = \frac{4d_3}{L+L'} \cdot \frac{U_o}{U_2} \quad , \quad c = \frac{4d_3}{\sqrt{\frac{2qU_o}{M}}} \cdot \frac{U_o}{U_3}$$

$$p = \frac{U_2}{U_o} \quad \text{and} \quad K = \frac{U_1}{U_o}$$

we can calculate the total time of flight (from the grid U_{G_o} to the annular detector)

$$T_o = C \left[\frac{A_1}{\sqrt{K}} + A_1 n \left(\sqrt{K} - \sqrt{K-p} \right) + \sqrt{K-p} \right] \tag{1}$$

The focussing conditions which are obtained by derivating $T = f(K)$ to the second order are $A = \sqrt{3}$ and $p = \frac{2}{3}$ for $n \ll 1$.

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In that case, equation (1) reduces to :

$$T_1 = \frac{C\sqrt{3}}{3} (4 + n \sqrt{3} - 1) \tag{2}$$

However, in the present system, ions are accelerated on the distance d_1 by the acceleration voltage U_o. The total time of flight is therefore :

$$T = T_1 + T_{acc} \tag{3}$$

with
$$T_{acc} = \frac{2c.A.d_1}{L + L'} \; (\sqrt{K} - \sqrt{K-1})$$

and the reflexion can only compensate the free field space T.O.F. The only possibility to attenuate the time dispersion in the acceleration region is to increase the total T.O.F. distance.

II. RESULTS

Fig. 3 shows the T.O.F. peaks of negative ions of I^-, $(CsI_2)^-$, and Cs^+ emitted from a thin cesium iodide deposit. The resolution at half maximum $T/\Delta T50\%$ is 4.500, which therefore gives a mass resolution

$$\frac{M}{\Delta M_{50\%}} = \frac{1}{2} \; \frac{I}{\Delta T} \cong 2250 \;.$$

Heavier clusters have also been observed in the spectra with a similar mass resolution.

For these atomic ions and clusters we have measured the efficiency of the mirror defined as $\rho = \frac{N_{reflex}}{N_{direct}}$, N_{direct} beeing the number of ions of a given type detected for a certain time t with the spectrometer operating in the direct mode (no bias on the reflecting grids and electrodes), N_{reflex} beeing the number of the same type of ions detected for the same time t by the annular detector (see fig. 1) with the mirror in operation. Values of ρ were rather constant and around 30 ± 5 % when the mirror is perfectly adjusted. Let us recall that ions have to pass 2 times through 2 grids and this already reduces the transmission down to 63 % (90 % transparency by grid).

The "reflexion " has also been tested with large organic molecules like "nigericin" (M.W = 724) which had been previously studied with a direct T.O.F. system (25). The molecular ion region is shown in Fig. 3, which indicates the presence of M + Na and M + 2Na - H peaks with a clear separation of the ^{13}C isotopic peaks. In this case of organic compounds the mass resolution at half maximum is around 2500 and the efficiency is comparable to that of inorganic ions. Spectra were recorded and analysed in a few minutes with a small computer.

CONCLUSION

These first results demonstrate that rather good mass resolution can be obtained with a [252]Cf time of flight mass spectrometer without changing drastically the total efficiency. High stability voltage power supply fast timing electronic and precise or adjustable mechanical alignments are necessary to obtain these performances (24). Further experiments are performed
                                         for much heavier molecules*
with the objectives of achieving a better mass resolution but also to assess the potential of the apparatus for metastable reaction studies. Two T.O.F. spectra can be recorded simultaneously : neutrals in the direct spectrum and ions in the reflex spectrum. Fig. 5 shows an example of this type of measurements performed for the molecule adenosine. Furthermore, a direct (neutrals + ions) spectrum can also be obtained in a different measurement. The comparison and the correlation of these spectra recorded event by event should certainly be extremely useful to elucidate fragmentation mechanisms and related processes.

This technique could also be applied easily to time of flight mass spectrometry using laser and K.e.V. ions (or neutral) for ionisation-desorption processes provided that the duration of the start pulse signal be shorter that 3 nsec.

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* note added in proof : The same resolution has been achieved for molecule with mass around 3000 and a separation of isotopic peaks is clearly visible (24).

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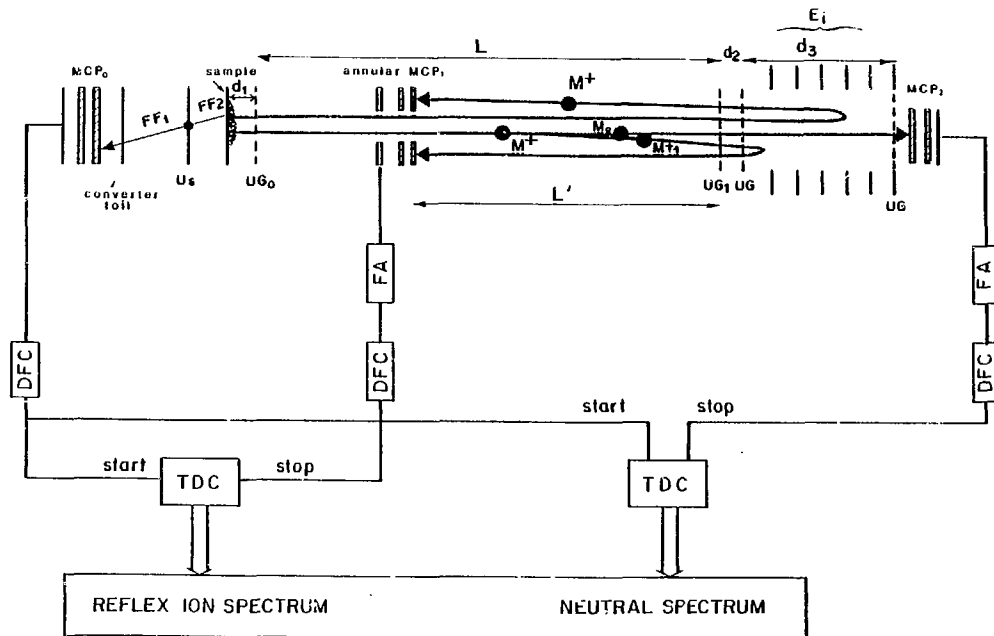
Figure 1 : Schematic diagram of the time of flight spectrometer. Trajectories
of ions and neutrals are indicated.
Experimental parameter values : $d_1 = 4$ mm, $d_2 = 5$ mm, $d_3 = 90$ mm,
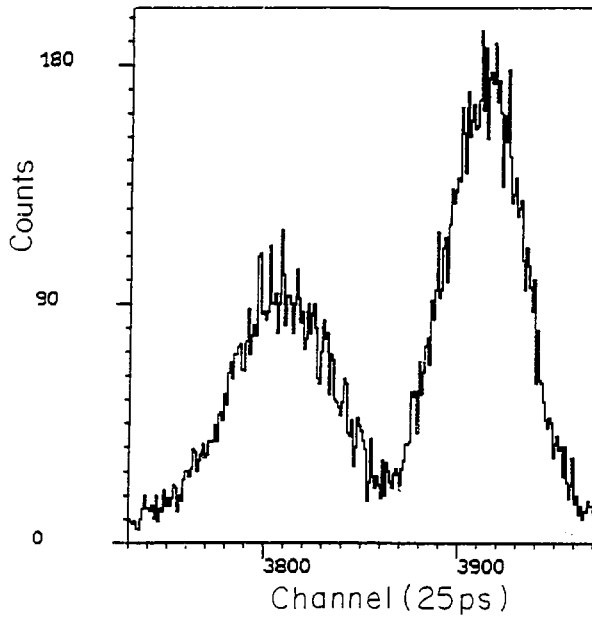$L = 920$ mm, $L' = 610$ mm, $U_{G_3} = 8$ KV.

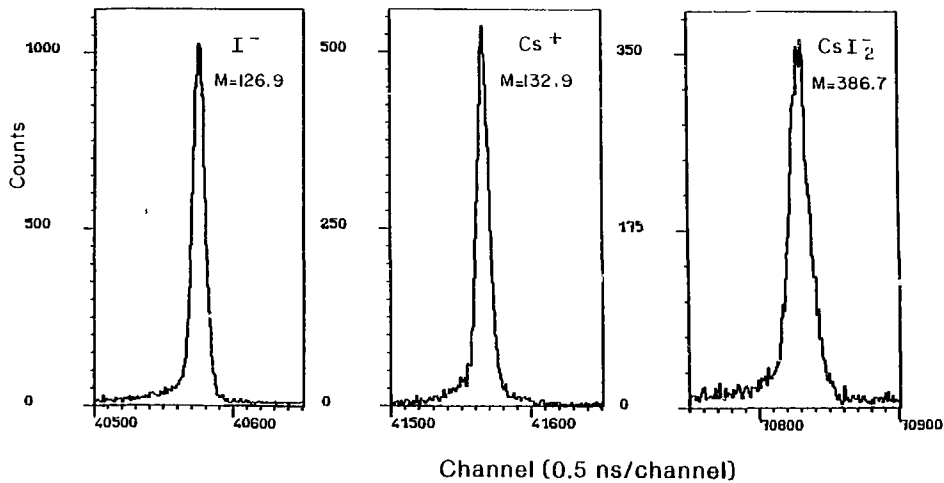Figure 2 : Time distribution of the fission fragment times of flight (see text).

Figure 3 : Time of flight peaks of I⁻, CsI⁻, Cs⁺ emitted from a CsI deposit $\frac{T}{\Delta t_{50\%}} \sim 4500$ (5 ns FWHM for Cs⁺).
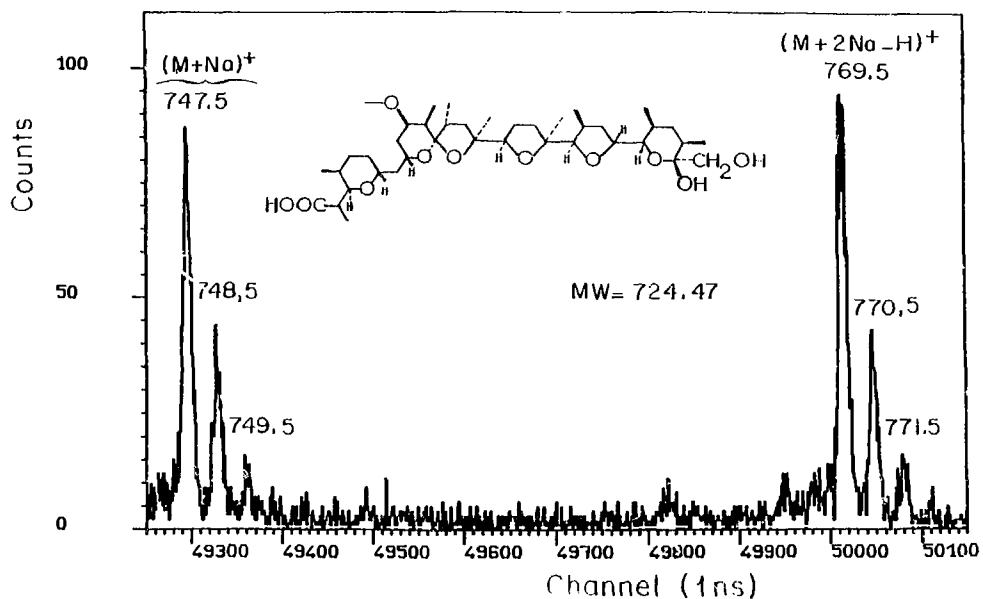
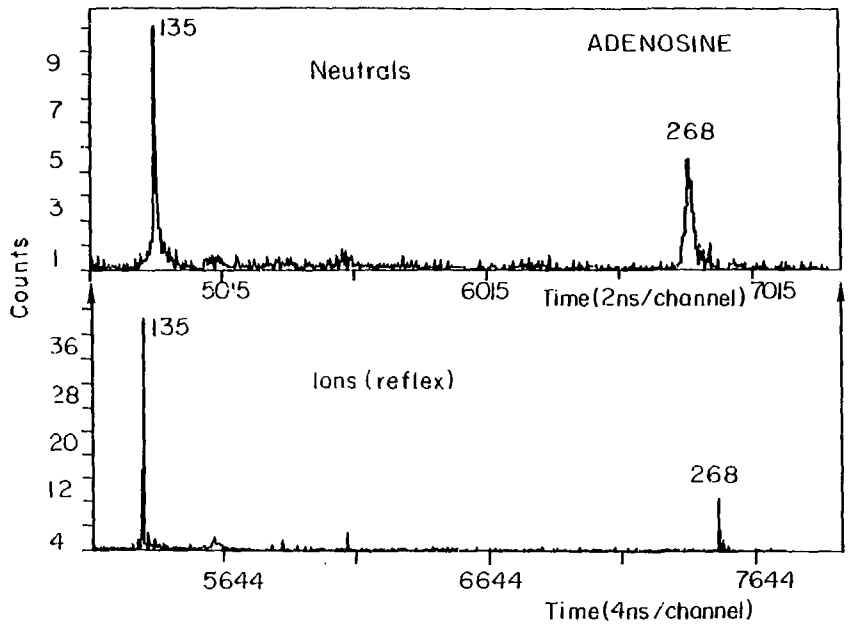Figure 4 : Ion molecular mass region of the Nigericine reflex time of flight spectrum. $\dfrac{T}{\Delta t_{50\%}} \sim 5000.$ ($\leq$ 10 ns FWHM for M $\approx$ 769).

Figure 5 : Spectrum of neutrals and ions.