# A High-Resolution Time-of-Flight Mass Spectrometer Using Laser Resonance Ionization

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Z. Naturforsch. **40a,** 1349–1350 (1985);
received December 2, 1985

A resonance ionization time-of-flight mass spectrometer is presented and mass spectra are shown which demonstrate its analytical capability, i.e. the possibility of soft and hard ionization, the wavelength selectivity and the mass resolution of 6500 (50% valley) at mass 96, which is expected to increase much more at higher masses.

A drastic increase of the mass resolution for time-of-flight (TOF) mass spectrometers could be obtained in recent years. They are now the systems of choice for many applications in combination with pulsed ionization processes due to their special features – generation of a complete mass spectrum for each ionization pulse, production of many mass spectra per second, an unlimited mass range.

The improved mass resolution is the result of the utilization of ion sources which provide precisely defined ionization time, ionization region and a small initial velocity spread, and of the application of new "time focusing" methods which reduce the time spread of ions with different energies. A very efficient method to compensate for the flight times of ions with different energies is the use of an electrostatic ion reflector [1, 2]. It permits higher energy ions to penetrate deeper into the reflecting field and so to spend there a longer time such that their shorter flight times in the drift regions are compensated.

We have developed a new ion reflector which in contrast to the above mentioned Mamyrin type ion reflector [1] represents an ion optical system without any metal grids, which accomplishes not only time compensation with respect to different ion energies but also geometrical focusing of the entering ion beam. It is mechanically simpler and should have a higher transmission and a higher mass resolution due to the lack of perturbing effects of the grids. Other theoretical approaches to a gridless ion reflector based on a different design have been published [3, 4].

Optimal ion source conditions for high mass resolution are provided by laser ionization due to the small focus (0.1 mm wide) and short pulse length (5 nsec) of currently available laser beams.

If in addition tunable laser radiation is used to provide the so-called resonance-enhanced multi-photon ionization, such a system has some further properties which are of special value for analytical purposes [2]:

(i) Selective ionization of one component of a mixture can be achieved by tuning the laser wavelength to spectral regions where efficient absorption and ionization only of this component occurs. This refers also to the selection of isotopic or isomeric species in as far as their spectral structures differ from each other.

(ii) Soft ionization generating only parent molecular ions or hard ionization to yield a pattern of strong fragmentation can be set up by controlling the laser pulse power; these are valuable methods for molecular weight determination and for structure analysis, respectively.

The multi-photon ionization mass spectrometry introduced in 1978 [5], provides quasi a two-dimensional analysis method, selective with respect to wavelength and mass.

A schematic diagram of the laser time-of-flight mass spectrometer is shown in Figure 1. The vapor sample is injected into the ion source through a small tube of 0.15 mm inner diameter. In front of the tube the ions are produced by irradiating the effusive beam of molecules by pulsed laser light from a dye laser whose wavelength is tuned to a resonant transition of the molecules. The dye laser is pumped by an excimer laser operating at 308 nm wavelength. For many molecules to be efficiently ionized it is necessary to operate the instrument in the ultraviolet wavelength region using a frequency doubling system.

The ions produced in the focus volume of 0.1 mm diameter are accelerated to a nominal kinetic energy of 700 eV. After passing a first drift region they are reflected by the ion reflector into a second drift region after which they hit a tandem microchannel plate detector. The detector output is fed into a transient recorder which is triggered by the laser photodiode output pulse. The digitized time spectrum is transferred to a computer for further processing. The mass spectra as well as the yield of all masses and of several mass regions can be displayed as a function of the wavelength, indicating the optimal wavelength regions for the analysis of the molecules of interest.

As an example for soft ionization mass spectra the mass spectrum of 2,5-Dimethyl-Furane is shown in Fig. 2, lower curve; almost only the parent ion mass is detected when a pulse energy of 0.08 mJ at 247.500 nm is used. Simply by removing the filter which eliminates the 495.000 nm fundamental wavelength a hard ionization mass spectrum with stronger fragmentation pattern has been recorded, i.e. by a pulse energy of 0.08 mJ (247.500 nm) + 4 mJ (495.000 nm), see Fig. 2, upper curve.

Figure 3 demonstrates the high mass resolution of the instrument together with the capability for selective ionization. It shows sections of the mass spectrum of a mixture of equal parts of 2,5-Dimethyl-Furane and Fluorobenzene at different wavelengths. At 247.700 nm the two components of mass 96.058 amu and 96.038 amu respectively appear with equal intensities (Figure 3a). Their nominal flight time difference is 6.5 ns. The two components can clearly be separated. At 247.500 nm Dimethyl-Furane is the dominant mass (Fig. 3b), whereas at 252.100 nm only Fluorobenzene is detected (Fig. 3c). The peak width of the single component in the time spectrum is 5 ns (FWHH) which corresponds to a mass resolution of $m/\Delta m = 6500$

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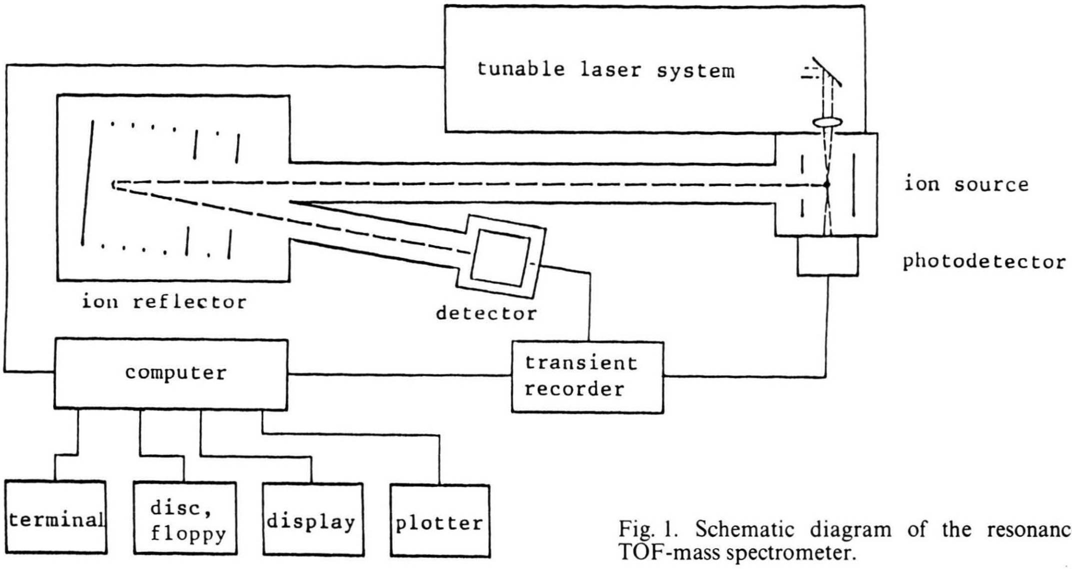

Fig. 1. Schematic diagram of the resonance ionization TOF-mass spectrometer.

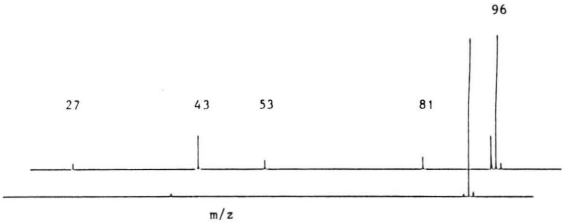

Fig. 2. Mass spectra of 2,5-Dimethyl-Furane at 247.5 nm laser wavelength; lower curve: soft ionization, $E = 0.08$ mJ/pulse; upper curve: hard ionization, $E = 0.08$ mJ (247.500 nm) + 4 mJ (495.000 nm) per pulse.

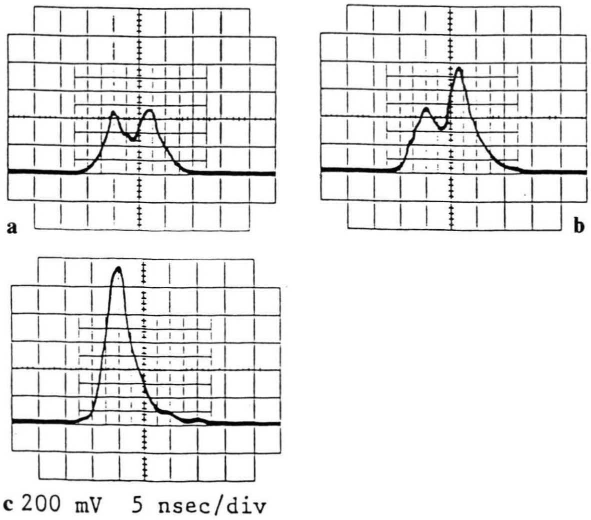

Fig. 3. Sections of mass spectra (storage oscilloscope scans) of a 50:50 mixture of 2,5-Dimethyl-Furane and Fluorobenzene, $E = 0.08$ mJ/pulse.
a) $\lambda = 247.700$ nm; b) $\lambda = 247.500$ nm; c) $\lambda = 252.100$ nm.

(50% valley) at mass 96. The absolute flight time of this component is 65.080 μs.

Obviously the peak width of 5 ns is mainly due to the laser pulse duration of 5 ns. With shorter laser pulses the mass resolution is expected to be even higher.

Assuming a constant peak width $\Delta t$ over the full mass range the mass resolution should increase according $m/\Delta m = t/2\Delta t$, i.e. proportional to the square root of $m$ and, e.g., reach a value of higher than 10 000 at mass 400. Of course problems must be solved providing vaporized molecules of low thermal energies to the ionization region.

These examples, showing the possibility of soft and hard ionization, the wavelength selectivity and a mass resolution of 6500 at mass 96 of the resonance ionization TOF-mass spectrometer, may demonstrate its capability as a powerful analytical tool.

### *Acknowledgement*

We thank H. Selzle, K. Sengteller and H. Fung for the computer program which could be used to calculate the ion trajectories and flight times for the design of the ion reflector.

We gratefully acknowledge financial support from the Bundesministerium für Forschung und Technologie, FRG.

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