Laser Tandem Mass Spectrometry in a Time of Flight Instrument

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We present a new laser tandem mass spectrometry technique in a reflectron time of flight (TOF) instrument. A first pulsed laser performs the multiphoton ionization and the primary photodissociation. A newly designed ion source permits a high mass resolution in the space focus of the 12 cm long first linear TOF, where then the secondary excitation can take place. For high resolution applications the pure secondary or pure metastable mass spectrum of a preselected precursor ion can be recorded using a new reflectron scanning technique. It is also possible to obtain the whole secondary mass spectrum with one cycle using a new postacceleration method. Several techniques for ejection of interfering ions are shown. The features of our techniques are demonstrated at various primary fragments of benzene.

Key words: Mass spectrometry, Time of flight instruments, Laser excitation, Photodissociation, Multiphoton processes.

I. Introduction

Tandem mass spectrometry (MS/MS) is one of the most sophisticated analytical techniques. Due to the variety of experimental arrangements MS/MS offers a wide field of applications from identification of complex mixtures to investigations of molecular structures and ion reaction kinetics in the gas phase [1].

The concept of tandem MS instruments combines a first mass spectrometer and a secondary excitation region with an energy filter or a second mass spectrometer. The most common MS/MS instruments are combinations of quadrupole and/or double focussing mass spectrometers. However, these instruments are essentially only employed with continuous ionization and excitation techniques like electron ionization (EI) and collisional induced dissociation (CID). Therefore a combination with the pulsed multiphoton ionization (MUPI) and multiphoton dissociation (MPD) techniques is not practical. The multiphoton ionization technique offers many advantages like species selective ionization, soft ionization even of fragile molecules, a variable degree of fragmentation and a large amount of metastable ions. Ion cyclotron resonance (ICR) mass spectrometers allow MS^n-experiments and can be combined with MUPI but they represent a rather complex method with low repetition rate.

Time of flight (TOF) mass spectrometers on the other hand are ipso facto adapted to pulsed multiphoton ionization. Due to the success of pulsed desorption techniques TOF-instruments with their unlimited mass range, high transmission and fast repetition rate are also the systems of choice for investigations of nonvolatile, thermally labile biomolecules [2], a field of rapidly growing interest.

The renaissance of TOF mass spectrometers in the last decade is mainly due to the drastically improved mass resolution which now exceeds 10 000 [3, 4]. This was achieved by the development of the reflecting field geometry [5] which is now adapted to Tandem-MS requirements by our new scanning technique.

Expansion of the TOF philosophy to a tandem MS configuration with a high mass resolution is difficult. There exist already TOF-MS/MS concepts that have been performed with secondary laser excitation, as by our group directly in the ion source [6, 7], by Lineberger et al. [8] in the field free drift region, or by Duncan et al. [9] in the ion mirror of a reflectron. However, all these experiments suffer more or less from the relatively low mass resolution ($M/\Delta M \leqq 200$) in the first and/or second stage.

We combine here a new linear TOF and a modified reflectron TOF (RETOF) to an MS/MS instrument. A special new ion source now permits in the linear TOF a time of flight correction of second order for variations of the ion energy simultaneously for all masses, in contrast to a correction of first order known so far. This improves the mass resolution of the first stage.

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The second stage of our arrangement maintains in principle its good mass resolution, typical for RETOF instruments, for all secondary masses due to a special tuning mode of the ion mirror. With this technique it is possible to observe either pure metastable mass spectra without secondary excitation or pure secondary excitation mass spectra. For the elimination of interfering signals a deflection technique with high mass resolution in the "space focus" as well as difference measurements were performed.

We will demonstrate these features of our new method at various metastable and secondary fragmentation spectra of the benzene cation and primary benzene fragment ions.

II. Experimental Techniques

In this section we describe our new MS/MS laser TOF apparatus (see Figure 1). It consists of a linear TOF with laser ionization source, the secondary excitation region at the "space focus" with the possibility of post acceleration, and the reflectron mass analyzer with field free drift region, ion reflector and ion detector.

In the following sections we distinguish between primary ions, primary metastable ions and secondary ions. Primary ions are produced in the ion source by laser 1. Primary metastable ions are primary ions with high internal energy decaying in the field free drift region. This high internal energy is caused by further excitation of the primary ion by laser 1. The secondary fragment ions are produced by secondary excitation by laser 2.

1. Secondary Excitation at the Second Order "Space Focus"

One key part of our new apparatus is the secondary laser excitation at the "space focus" of the first, linear, TOF. This "space focus" is a point where the time of flight is to a certain degree independent of variations of the kinetic ion energies. This means that ion bunches consisting of the same mass but differing in kinetic energy show here an optimum of longitudinal spatial and equivalently an optimum of time compression. Space focusing with a correction of first order has previously been used by Wiley and McLaren [10] for increasing the mass resolution of linear TOF instruments. However, by combining it with time-lag-focusing [10] in the Wiley McLaren type TOF analyzers, the conditions for energy correction become mass dependent, in other words, the position of the "space focus" is shifted for different mass numbers. This time-lag-focusing has been introduced to compensate large initial kinetic energies.

In the usual one-stage ion source (two electrodes) the distance *c* (see Fig. 1) between the attracting electrode and the "space focus" is just twice as large as the distance *a* between the point of ionization and the

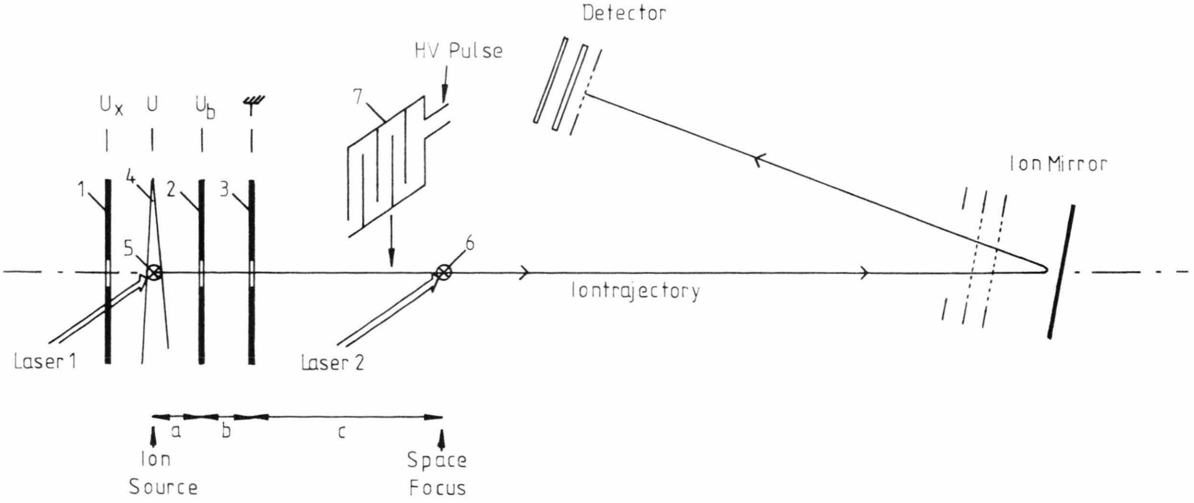

Fig. 1. Experimental setup with ion source, secondary excitation within the "space focus", fieldfree drift region, ion reflector and ion detector. 1, 2, 3: electrodes of the ion source, 4: molecular beam, 5: focus of laser 1 (ionization), 6: focus of laser 2 (secondary excitation), 7: arrangement of wires for deflection of ions by pulsed fields.

attracting electrode. By using a two-stage ion source (Fig. 1, three electrodes) the distance to the "space focus" is no longer fixed but can be shifted to larger values of c. So it is possible to increase the time of flight from the point of ionization to the space focus, thus reducing the influence of the laser pulse width and the detector response time on the mass resolution. First order focusing conditions for different arrangements of electrodes have been investigated theoretically by Sanzone [11], but no improvement has been found in comparison with a two-stage ion source.

Instead of a first order "space focus" known so far we developed now an ion source with a "space focus" of second order correction. This allows for compensation of much larger variations of the kinetic ion energy due to the spatial distribution in the extraction field. Therefore, in analogy to a two-stage ion reflector that also corrects in second order, a second order "space focus" enables considerable enhancement in mass resolution. Rather than the spatial compression of the ion bunches, the spatial and temporal characteristics of the laser pulses are now the factors limiting the mass resolution. For an ideal two-stage ion source (no field distortions or space charge effects) with second order correction, all geometric distances and potentials are determined (in analogy to the correction conditions of a reflectron [5]) by

$$a = \frac{c-2b}{2(c+b)}\left(c\cdot\left(\frac{c-2b}{3c}\right)^{3/2}+b\right), \qquad (1)$$

$$U_b = U_{\mathrm{tot}}(2c+2b)/3c\,. \qquad (2)$$

The repeller voltage U_x is therefore

$$U_x = U_{\mathrm{tot}}\,[(2c+2b)/3c + x/a\,(c-2b)/3c]\,. \qquad (3)$$

A typical set of ion source parameters obeying (1) and (2) is: $a = 1.0$ cm, $b = 0.8$ cm, $c = 11.2$ cm, $U_b = 500$ eV and $U_{\mathrm{tot}} = 700$ eV (see also Figure 1). For such a configuration, ions with mass 100 have a time of flight to the "space focus" of 4.5 μsec. With a laser pulse width Dt of 5 ns a mass resolution $R(50\%) = 1/2 \cdot t/\mathrm{D}t$ of 450, and with a 2 ns laser pulse a resolution $R(50\%)$ of 1100 can be achieved, provided the focus size of laser 2 is smaller than 140 μm for the former and 55 μm for the latter case; this is easily achieved by focusing commercial tunable dye lasers with lenses of 10 cm focus length.

2. *Elimination of Single Masses*

We introduced a technique to deflect ions of a single mass or of a range of masses from the mass spectrum. This is performed by a pulsed electric field near the "space focus". This pulsed field is produced by an arrangement of parallel wires (see Figure 1). Complementary high voltage pulses ($U = +/-200$) are applied to set 1 of wires (+) and set 2 (−). Thus a transversal deflection of all ions which pass this net of wires during the high voltage (HV) pulse is achieved. By adjusting the time delay between this HV pulse and the ionization, single masses or a range of masses can be eliminated from detection. This set of wires builds a spatially defined deflection area and allows therefore an elimination with considerably higher mass resolution than deflection plates as used e.g. by Duncan et al. [9] and Zare et al. [12]. The resolution obtained with the deflection grid fits well with the high mass resolution at the space focus.

With this technique the following problem can be solved: Primary metastable ions decay in the whole drift region to various fragments. These products have similar kinetic energies as fragments due to secondary excitation in the field free drift region and would therefore severely interfere with secondary mass spectra. So it is necessary to eliminate all precursor ions of strong metastable decay and their products. These products have the same velocity and therefore the same arrival time at the wire net as their precursor ions. Thus, by eliminating primary ions of a certain mass all their products, due to metastable decay, are simultaneously eliminated.

3. *Difference Measurements*

However, if the ions of interest for a secondary excitation are themselves metastable (decaying due to the primary excitation in the ion source) the pulsed elimination of their products is of course not applicable. For this case, as well as for the case that other primary fragments cannot be eliminated completely, a difference measurement is additionally used. Here we switch the second laser on and off so that secondary excitation only takes place for every other ionizing pulse of laser 1. By subtracting the ion signals with laser 2 on and off, all ion signals contributed solely by primary excitation can be eliminated. Combination with method 1 avoids subtraction of too intense ion signals which would cause signal fluctuations.

4. *Secondary Mass Selection with a Post Acceleration Technique*

With the postacceleration technique the complete secondary mass spectrum of one preselected ion can be recorded during one cycle. Secondary fragment ions as well as the products of a metastable decay are produced in a field free drift region. Their kinetic energy (E_F) therefore depends on the ratio of daugther (m_F) to precursor (m_M) ion mass:

$$E_F = E_M \cdot m_F/m_M, \quad E_M = q \cdot U_{tot}. \qquad (4)$$

This results in a large energy distribution of the secondary masses which cannot be corrected by an ion reflector using conventional operating conditions. With a post acceleration after the "space focus" it is possible to add a constant energy (E_P) considerably larger than E_M to all ions. Now the relative energy differences between the secondary ions of different mass are small enough for a time of flight correction in the reflectron. The primary mass spectrum, which would interfere with the secondary mass spectrum, can be eliminated by decreasing the voltage of the reflector end plate to a value slightly lower than $(E_M + E_P)/q$. Thus all ions with full kinetic energy (i.e. all primary ions) will strike the reflector end plate.

5. *Secondary Mass Selection with a Reflector Scanning Technique*

In principle, the reflector scanning technique allows the recording of a secondary mass spectrum with the excellent mass resolution typical for RE* mass spectrometers with little (<5%) energy distribution. The RE parameters for a second order time correction are also given by (1) to (3). They are not changed if all distances are passed two times, only the corresponding variables have to be exchanged, i.e. "x" is the length of the reflector field, "a" is the "intruding depth" into the reflector, "b" is the length of the retarding field and "c" is again the field free drift region, but now between "space focus" and ion reflector. U_b and U_x are the potentials of the retarding field and the reflector end plate, qU_{tot} is the kinetic energy of the ions. The conditions for the second order correction show that the optimal intruding depth into the reflector field, (1), depends only on geometry factors, not on mass or energy. The optimal reflector voltage settings, necessary for this intruding depth, on the other hand, are also independent of the mass but are proportional to the kinetic ion energy. The relation between U_x and U_b, however, again depends only on the geometry of the instrument. If now the relation of the retarding to the reflector voltage is kept constant while reducing their absolute value, all secondary fragments with different energies (i.e. masses, (4)) are swept one mass after the other through the optimal correction.

If the kinetic energy release is small, the time of flight in the drift region is constant for all fragments of one precursor. The intruding depth, and therefore the time of flight in the ion reflector, also becomes the same for all fragments of one precursor if their optimal correction conditions are adjusted. Therefore, if the reflector voltage is scanned, all masses of one precursor (constant E_M/m_M) have the same time of flight at their optimal corrections which is exactly the time of flight of the precursor at its optimal correction. So it is possible to record all secondary fragments of one precursor within one fixed time gate by scanning the reflector potentials. The adjustment is simply done by using normal reflector voltages and setting the gate to the time of flight of the precursor ion in the primary mass spectrum.

III. Experimental Setup

For our experiments we used a homebuilt RETOF instrument with a two stage (three electrodes) laser ionization source optimized for a second order "space focus" about 10 cm downstream from the third electrode of the ion source (see Figure 1). An ion reflector was constructed with two grids and a depth of the reflecting field as short as possible, but still fulfilling the second order correction conditions. An excimer laser pumped dye laser was used for ionization and the third harmonic (355 nm) of a YAG laser for secondary fragmentation. In principle the instrument is similar to experimental setups used in other work of our group [3, 13]. The main difference is a further pair of vacuum windows allowing the second laser to be focussed onto the "space focus" of the ion source, a system of wires near the "space focus" and the capability of tuning the reflector. This apparatus is distinguished by its simplicity in comparison with other MS/MS techniques.

The dye laser (laser 1) emitted with a repetition rate of 40 Hz and the YAG laser (laser 2) with a repetition rate of 20 Hz, such that every other ionization pulse of laser 1 was followed by a fragmentation pulse of laser 2 with a time delay of 4 to 5 μs and a jitter of less than 2 ns. Both types of ion signal were recorded in a gated integrator with signal inversion switched on for every other laser shot, thus forming a difference spectrum of secondary and residual primary ions. The delay and width of the time gate for the ion detection

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* RE → RETOF.

was set to overlap with the signal of the particular ions of the mass chosen for secondary excitation. The reflector potentials have been optimized for primary ions (high kinetic ion energy). These reflector potentials are then the starting point for scanning the reflector fields while recording within the preset time window. An intrinsic feature of subtracted spectra are negative peaks due to those primary ions that are dissociated by the secondary excitation (laser 2).

For ionization of benzene a wavelength of 258.7 nm has been used. A primary mass spectrum (Fig 2a) with a medium degree of fragmentation comparable to electron impact ionization was produced by focussing the light (300 μJ pulse energy) with a lens of 15 cm focal length. By varying the laser pulse intensity, higher degrees of fragmentation can be achieved [6, 14]. Thus the yield of the ionspecies selected for secondary excitation can be optimized. All primary ions are accelerated to a final kinetic energy of 700 eV. After 2.7 μs the $C_3H_x^+$ group passes the "space focus", after 3.0 μs the $C_4H_x^+$ group and after 3.8 μs the molecular ion $C_6H_6^+$.

IV. Results

We wish to demonstrate our new technique employing benzene as an example. In order to test the primary mass resolution at the space focus we introduced a microchannel plate detector at this point. The region of mass 77–79 is shown in an expanded scale in Figure 2. The peak width (FWHM) of the benzene signal is 6.5 ns, limited by the laser pulse width. The time difference between the masses 78 and 79 is 61 ns, which results in a mass resolution of 720 for the primary mass spectrum at the space focus. This is an excellent value for a TOF instrument with 12 cm drift length and demonstrates the usefulness of this new instrument. The ion energy was here 440 eV.

Typical features in a multiphoton mass spectrum of benzene with medium fragmentation are the dominating $C_4H_3^+$ in the $C_4H_x^+$ group and the dominating $C_3H_3^+$ in the $C_3H_x^+$ group. This can be seen in Fig. 3a, where the primary mass spectrum is shown. By setting the time gate at mass 78 (35 μs) and scanning the reflector voltages without using laser 2 and the difference measurement, the mass spectrum of the metastable decay of benzene is recorded. This spectrum is shown in Figure 3b. By firing laser 2 at the appropriate time (3.84 μs) the secondary mass spectrum of benzene is observed (Figure 3c). The typical features of the primary mass spectrum are even more pronounced in the secondary mass spectrum of $C_6H_6^+$. This is probably due to the longer wavelength of 355 nm. The pulse energy of the second laser was 50 mJ.

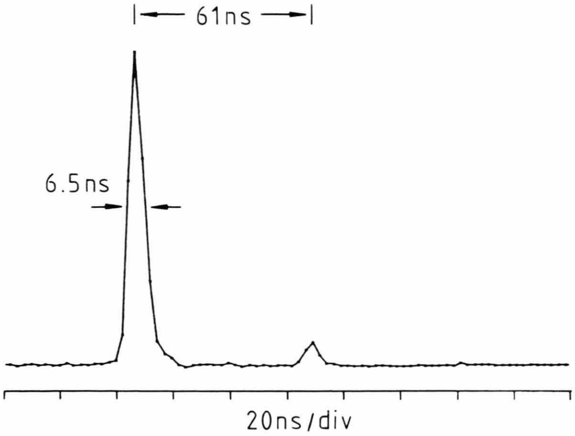

Fig. 2. Part of the primary time of flight spectrum of benzene recorded at the "space focus". The masses 78 and 79 are shown; the mass resolution is 720 (FWHM).

Secondary mass spectra of primary fragment ions are shown in Figure 4a, b. In Fig. 4a the mass spectrum resulting from the secondary excitation of $C_4H_2^+$ is presented. The main fragments besides C_4H^+ and C_4^+ are C_3H^+, C_3^+ and a smaller amount of C^+. No member of the $C_2H_x^+$ group has been observed. The insert shows the expanded region of mass 36–37. From these data the mass resolution of this secondary spectrum can be calculated to be about 350 (50% valley). At present the resolution of our secondary mass spectrum is limited to this value by the minimal step of the voltage scan possible with our HV-power supply. By scanning with smaller steps, the resolution should reach the limits typical for reflectrons. The dip at mass 50 is of course due to the difference measurement. The intensity of the precursor ion with mass 50 is decreasing and causes therefore a negative signal. In Fig. 4b the secondary mass spectrum of C_3^+ is shown. Here the fragmentation mainly results in the formation of C^+ and less C_2^+.

In principle, these two examples of secondary photodissociation of primary fragmentations demonstrate the possibility to follow step by step the fragmentation pattern of the benzene cation caused by multiphoton dissociation.

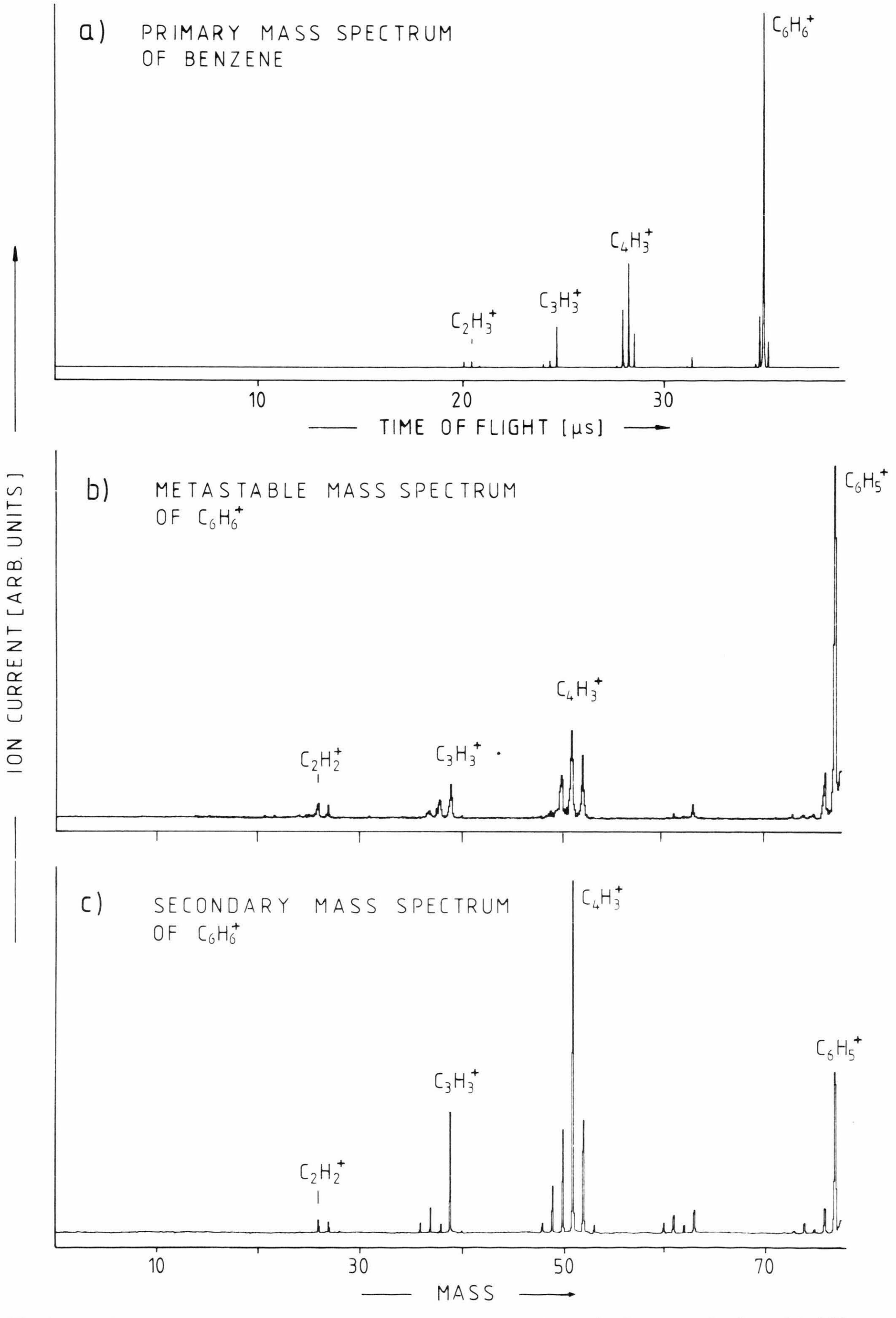

Fig. 3. a) Primary time of flight spectrum of benzene induced by multiphoton ionization with 258 nm and 40 MW/cm^2. – b) Metastable mass spectrum of $C_6H_6^+$, note the linear mass scale. – c) Secondary mass spectrum of $C_6H_6^+$, secondary fragmentation is induced by light with $\lambda = 355$ m.

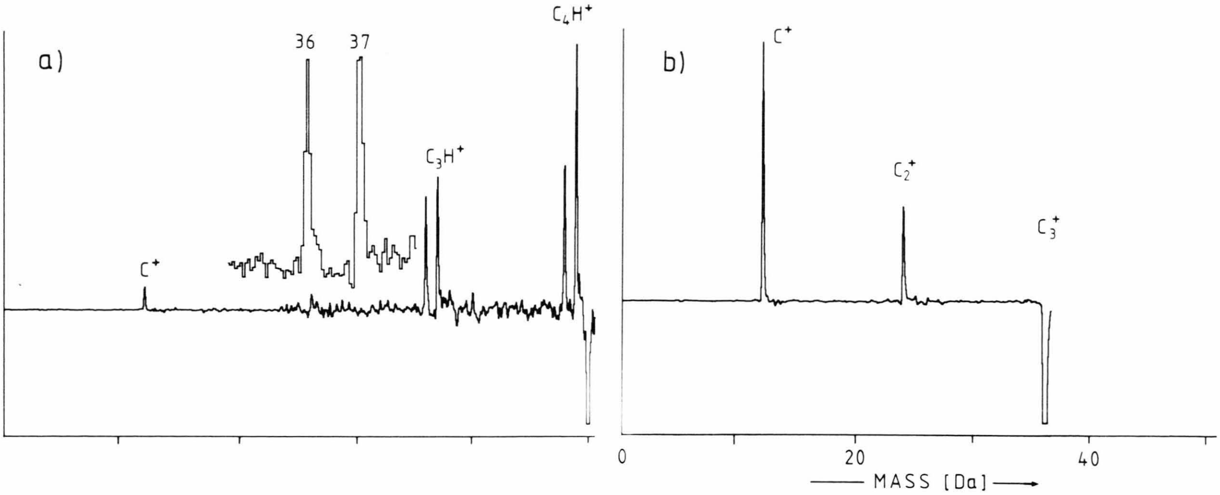

Fig. 4. Examples of secondary mass spectra of primary fragments: The preselected primary ions are a) $C_4H_2^+$ and b) C_3^+. Laser wavelength was 355 nm, laser power 50 mJ. The insert of Fig. 4a shows the masses 36 and 37 in an expanded presentation. The mass resolution R is about 350 (FWHM).

V. Conclusion

We have presented a new technique for tandem mass spectrometry in a time of flight instrument with laser ionization and laser dissoziation. Preliminary results on the example of benzene show the high mass resolution which is unique for TOF MS/MS techniques. A new ion source design allows the correction of time of flight broadening due to energy variation of up to second order at the "space focus", where the secondary excitation takes place. This instrumentation should therefore offer promising features for the investigation of fragmentation mechanisms and for the elucidation of ion structures.

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