A High Pressure Pulsed Expansion Valve for Gases, Liquids, and Supercritical Fluids

C. Köster, J. Grotemeyer, and E. W. Schlag
Institut für Physikalische und Theoretische Chemie, Technische Universität München, FRG

Z. Naturforsch. **45a,** 1285–1292 (1990); received October 18, 1990

A novel design of a pulsed valve for coupling chromatographic techniques with gaseous and liquid mobile phases to a time-of-flight mass spectrometer with multiphoton ionization (MUPI) is presented. The valve can be operated in low pressure regions (<10 bar) up to temperatures of 350 °C and at higher pressures (300 bar) up to temperatures of 200 °C. Pulse widths lower than 100 μs could be measured. First results demonstrate the ability of interfacing of liquid chromatography to MUPI-mass spectrometry. Additional coupling of CO_2-laser desorption to the valve allows the interface to be used for mass spectrometric measurements of nonvolatile biomolecules.

Key words: High pressure valve, Chromatography, Multiphoton-ionization mass spectrometry.

Introduction

The advantages of multiphoton ionization (MUPI) in combination with time-of-flight mass spectrometry (TOF-MS) have been extensively described in [1]. This two dimensional mass spectrometry technique, with regard to the wavelength and photon intensity dependence in the mass spectrum, can be extended to a three dimensional technique by coupling with chromatographic methods. Due to the substance specific ionization process [2], the ionization and detection of signals from the mobile phase can be avoided. Therefore interferences in the low mass region of the mass spectrum due to the solvent will not occur. Further advantages to be expected are the reduction of sample amount required through time focussing by the chromatographic process and enhanced sensitivity due to the high ionization efficiency of the MUPI process.

An interface for coupling a chromatographic technique to a mass spectrometer normally represents a compromise, because of the great differences in working pressures and different phase behavior of these two techniques. Mass spectrometry depends heavily on good vacuum conditions with pressures typically below 10^{-5} mbar while liquid chromatography (LC) works best if the pressure is between 10 and 100 bar. This is especially true for coupling a continuously working chromatograph with an inherently pulsed TOF system.

Some years ago efforts were made to combine gas chromatography (GC) with TOF-MS using a pulsed valve [3]. The practicality of that system was limited to much by the non-consequent reduction of the dead volume of the used solenoid valve. Other groups inserted the heated end of a GC capillary column into the ion source of a TOF-MS [4], but here an effusive gas beam could only be produced. However, the MUPI process works optimal with spectroscopically cold molecules, obtained from a seeded supersonic beam [5].

In this paper, we present a complete new design of a pulsed valve with a nearly zero dead volume. To allow continuous working of the chromatograph, the mobile phase is directed through the valve and only a small split is pulsed into the TOF-MS and ionized by multiphoton absorption. This valve has been tested to pressures up to 300 bar and to temperatures of about 200 °C. It produces under these conditions well shaped pulses of 50–75 μs in width. The valve can also be used for other detection methods requiring pulsed ionization such as FT-ICR etc.

Further practical advantages of this device are the possibility of a fast sample change, a constant signal intensity for instrument optimization and MS measurements of nonvolatile biomolecules by additional combination of CO_2-laser desorption.

I. Experiment

a) System Setup

The complete experimental setup has been described previously [6]. It consists of a differentially pumped

---

Reprint requests to Dr. J. Grotemeyer, Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstr. 4, 8046 Garching, BRD.

0932-0784 / 90 / 1100-1285 $ 01.30/0. – Please order a reprint rather than making your own copy.

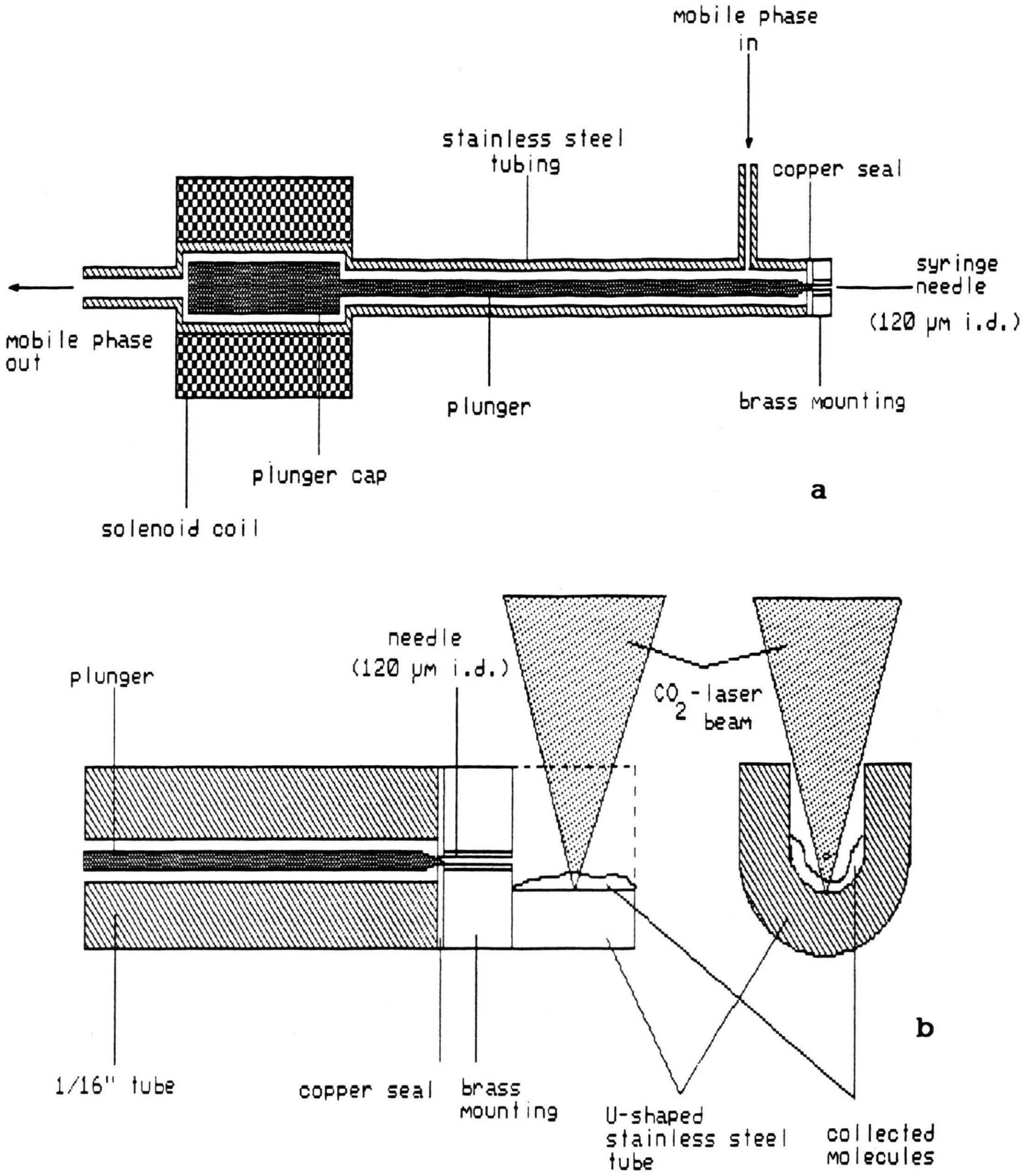


Fig. 1. a) Design of the pulsed valve. b) Details of the U-shaped tube surrounding at the end of the valve used for laser desorption.

vacuum system with a desorption chamber, laser ion source and a reflectron time-of-flight mass spectrometer. A molecular beam of neutral molecules is emitted through the pulsed valve which is described later. The volatilization of samples can be assisted by a CO_2-laser focussed onto a part of the valve. The evaporation chamber is pumped by a turbo molecular pump to maintain a pressure better than 10^{-3} mbar, even when liquids are introduced with repetition rates over 10 Hz. The evaporation chamber is separated from the ionization source by a skimmer. In the ion source an additional turbo molecular pump provides a vacuum of about 10^{-5} mbar. The ionization laser beam produced by a frequency doubled Lambda Physics FL 3001 dye laser pumped by a Lambda Physics LP 110 iCC excimer laser, is focussed into the ion source through a focussing lens with a focal length of 20 cm. The UV-beam ($I \approx 10^5-10^8$ W/cm^2 at 260 nm) intersects the molecular beam about 10 cm from the nozzle aperture. Thus, for proper synchronization, the excimer laser and, in cases where biomolecules were measured the CO_2-laser must be delayed with respect to the valve pulse. The ions produced by the MUPI-process were mass analyzed in the TOF-MS and recorded by a 200 MHz transient digitizer (LeCroy, model TR 8828 C). Finally the collected data were analyzed and saved by an VMEbus computer (Force, Focus-32).

b) Valve Design

The design of the pulsed valve is shown in Figure 1 a. It consists of two basic sections: a) the solenoid and b) the plunger or injection enclosure. The solenoid is taken from a commercially available valve (General Valve Corporation, ser.-no. 16, part-no. 9-280-900) together with the voltage supply and control unit. The nozzle plate of this valve is changed to carry a 5 cm long 1/16″ steel tube with an inner diameter of 0.5 mm. The tube serves as a slide for the plunger, which is made from a stainless steel wire with a diameter of about 450 µm.

The top end of the plunger is mounted to a spring loaded plunger cap. The plunger tip is polished to a nearly paraboloid shape and forms a metal-metal seal when seated in the exit aperture due to the force of the spring when the magnetic pulse is off. Close to the end of the 1/16″ tubing is a 0.5 mm hole, for connecting a GC capillary column or a LC column with the aid of a T-union (SGE, type SSUT/16). This device reduces the dead volume between the mobile phase inlet and the aperture to about 5 µl. With this design of the valve it is possible to create a split of the mobile phase. A fraction of the mobile phase is pulsed out and analyzed by the mass spectrometer, while the remainder flows through the solenoid section and is discarded.

One advantage of the described construction is the spatial separation of the solenoid and the valve nozzle, which allows the heating of the injection nozzle by a thermocoax heater placed around the T-union without heating of the solenoid. The nozzle consists of a 2 mm long section of a syringe needle with an inner diameter of 120 µm. This small tube is hard-soldered into a brass mounting and screwed to the T-union. To provide proper valve operation it is necessary to change the plunger length as well as the distance between the plunger cap and the solenoid. The plunger length can be changed indirectly by shifting the plunger slide in or out of its mounting on the nuzzle plate.

For introduction of gaseous and volatile probes or in coupling gas chromatography with mass spectrometry (GC-MS) high temperatures in low pressure regions are necessary. By using pure graphite ferrules, the valve assembly has been tested up to pressures of 10 bar (argon) and temperatures to approximately 350 °C. The temperature is measured by a Cr–Ni–Cr thermocouple fixed onto the T-union. The pulse width of the valve can be varied by adjusting the plunger arrangement and/or the voltage applied to the solenoid, but the pulse width is not appreciably affected by changes in pressure or temperature. Presently, a pulse width of 50 µs (FWHM) is measured by monitoring the benzene 6_0^1 transition signal intensity at 259.026 nm. The sample is injected from a seeded beam of argon at 8 bar and 25 °C as a function of the delay between the ionization laser and valve pulse (Figure 2 a).

Our valve is also suitable for coupling liquid or supercritical fluids to TOF-MS. In this application the fluids or gases are pressurized by a Brownlee labs syringe pump (Model MG). The sample molecules are injected as pure liquids or dissolved in a suitable solvent, through a Rheodyne injection valve into the pressurized eluent liquid stream. For high pressures an additional seal between plunger tip and the valve aperture is necessary to prevent leaking. This seal is a 100 µm thick copper plate with a 100 µm hole for the plunger tip. With this seal and the replacement of graphite ferrules by graphite/vespel ferrules [7] the valve can be operated with over 300 bar backing pressure and simultaneous temperatures over 200 °C. As shown in Fig. 2 b the pulse width of the valve increases to about 75 µs (FWHM) compared to the pulse width obtained with 8 bar backing pressure of 50 µs (Figure 2 a).

For substances with very low vapor pressure using the high pressure valve as described no mass spectrometric signal could be detected due to cluster building and aggregation of the molecules shortly after they are introduced into the vacuum system of the mass spectrometer. To volatilize these molecules into the gas phase we have changed the nozzle design of the valve. An additional 3 mm long and 2 mm i.d. U-shaped tube surrounds the valve aperture (Fig. 1 b) to collect the precipitated sample. In a second step, the molecules are desorbed by a CO_2-laser pulse (Pulse System, model LP 30) at a wavelength of 10.6 µm and injected in the next gas pulse. Here the desorbed mole-

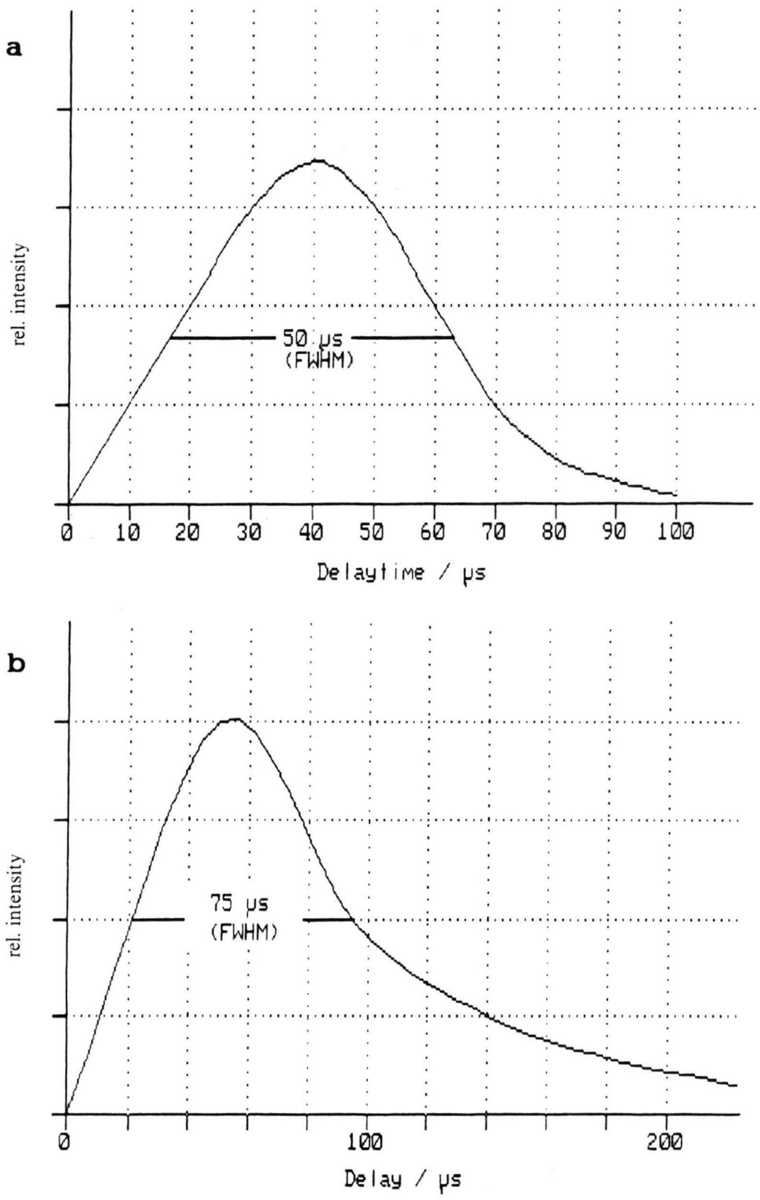


Fig. 2. Pulse profile of the valve monitoring the benzene 6_0^1 transition under different conditions. a) 8 bar argon backing pressure, nozzle temperature 25 °C; b) 100 bar methanol backing pressure, nozzle temperature 115 °C.

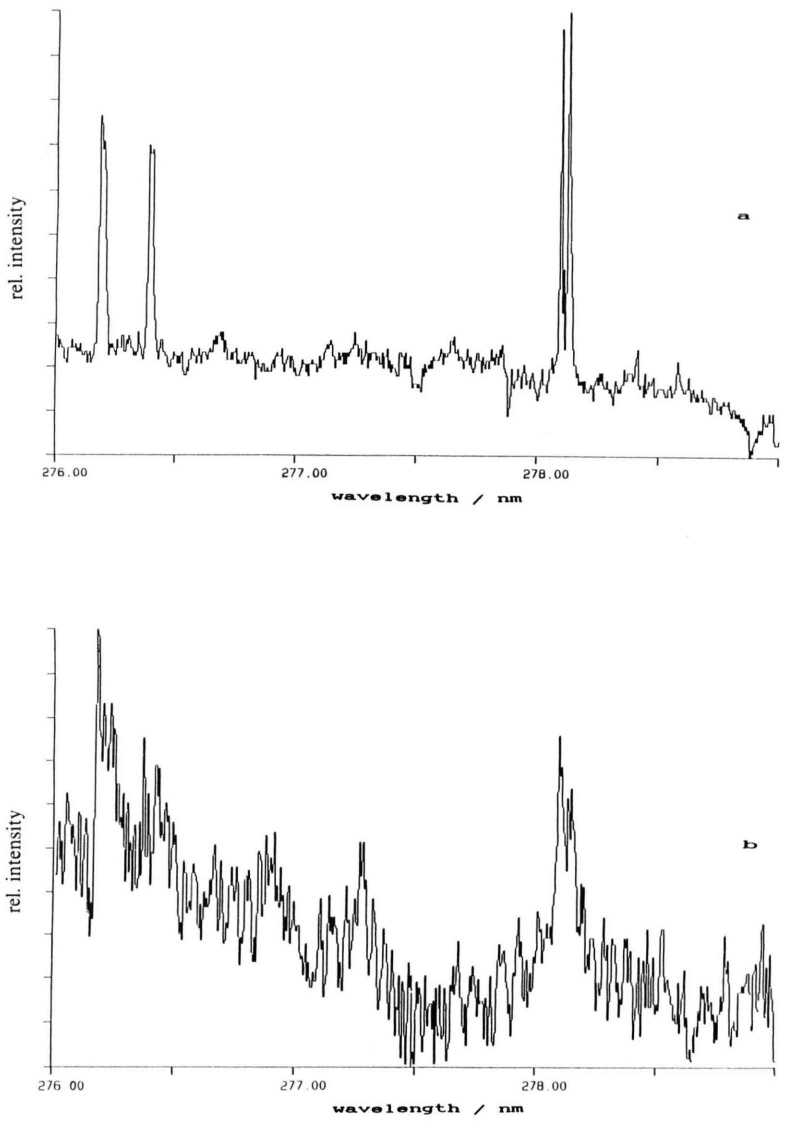
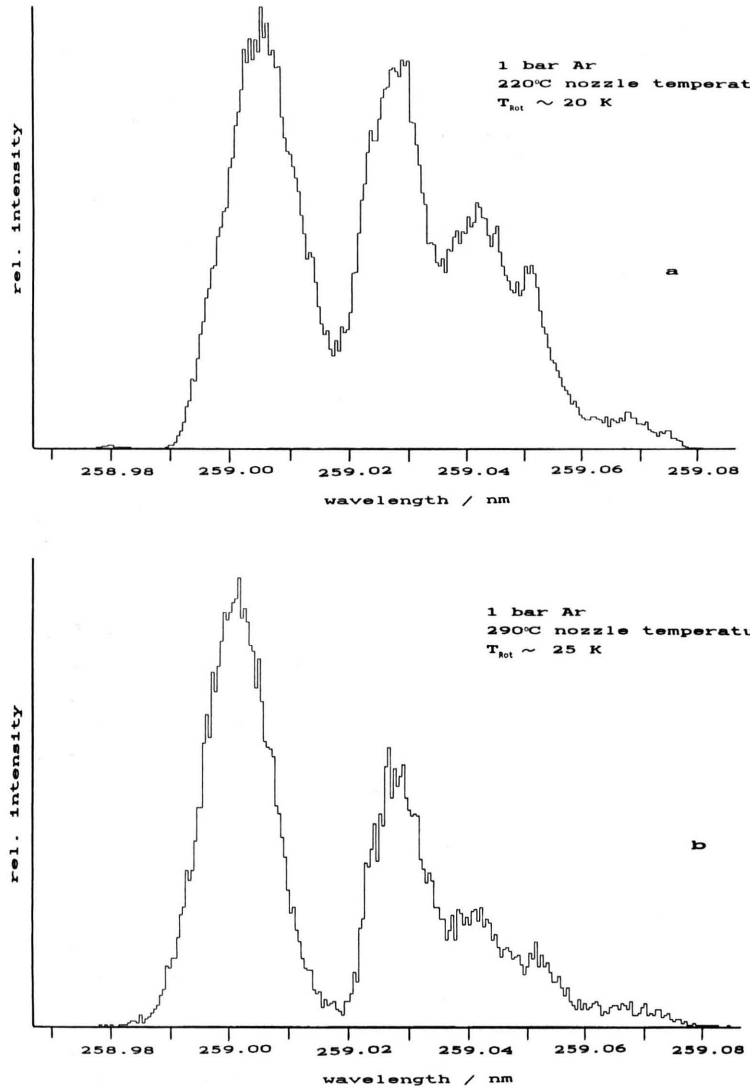


Fig. 4. Mass selected absorption spectra of the molecular ion of 1,3-dihydroxybenzene in the region between 276.0 to 279.0 nm under different conditions. a) Argon backing pressure 3 bar, nozzle temperature 125 °C, b) methanol



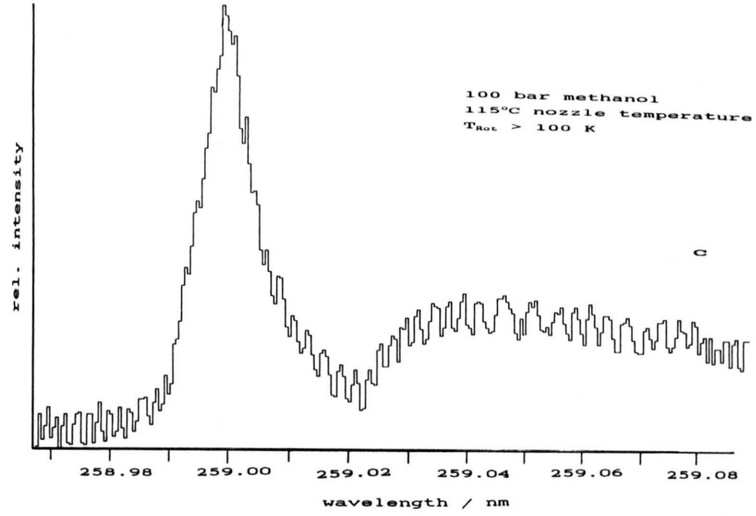


Fig. 3. Mass selected absorption spectra of the benzene 6_0^1 transition for different conditions. a) Argon backing pressure 1 bar, nozzle temperature 220 °C, $T_{rot} \sim 20$ K; b) 290 °C, $T_{rot} \sim 25$ K; c) methanol backing pressure 100 bar, nozzle temperature 115 °C, $T_{rot} > 100$ K.

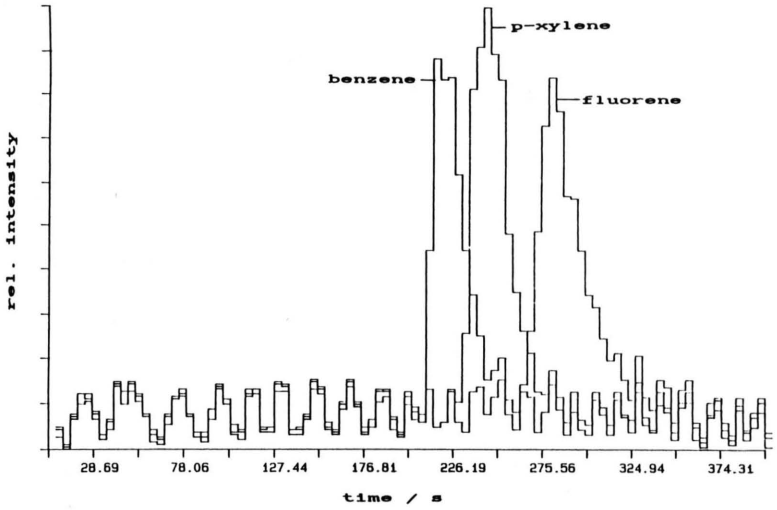


Fig. 5. LC-MUPI-MS monitoring of a solution with benzene, p-xylene and fluorene in methanol ionized at a wavelength of 259 nm.

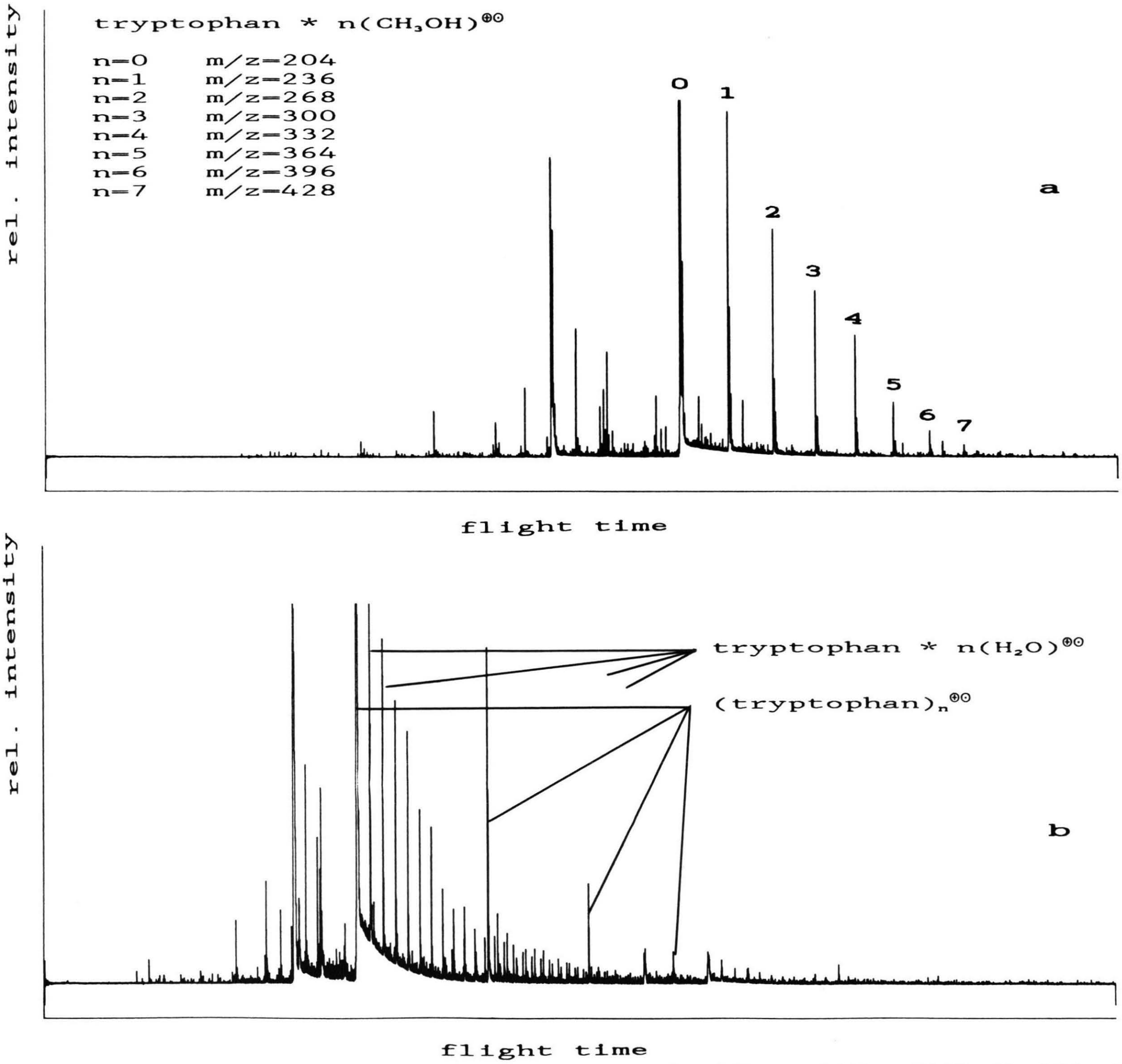


Fig. 6. Mass spectra of tryptophan obtained out of a solution in a) methanol, b) water (100 bar, 115 °C) with additional CO_2-laser desorption.

cules are cooled to a lower internal temperature and transported through the skimmer into the ion source. Figure 1 b shows the enlarged nozzle part of the valve supplied by the U-shaped collecting tube.

II. Results and Discussion

a) Gaseous Samples

The quality of the valve design is tested against the major criterion of the jet cooling achieved on different samples under different operating conditions. This criterion can easily be monitored by acquisition of the absorption spectrum of the gas phase sample. In Fig. 3 such 1+1 multiphoton absorption spectra are displayed. Here the benzene 6_0^1 signal is monitored from 258.98 to 259.08 nm. Spectrum 3a is taken with a nozzle temperature of 220 °C, while spectrum 3b is recorded at a nozzle temperature of 290 °C.

In both cases the backing pressure of the Ar gas stream was 1 bar. As seen from the comparison of both spectra the rise of the nozzle temperature has only a minor effect on the cooling and therefore the

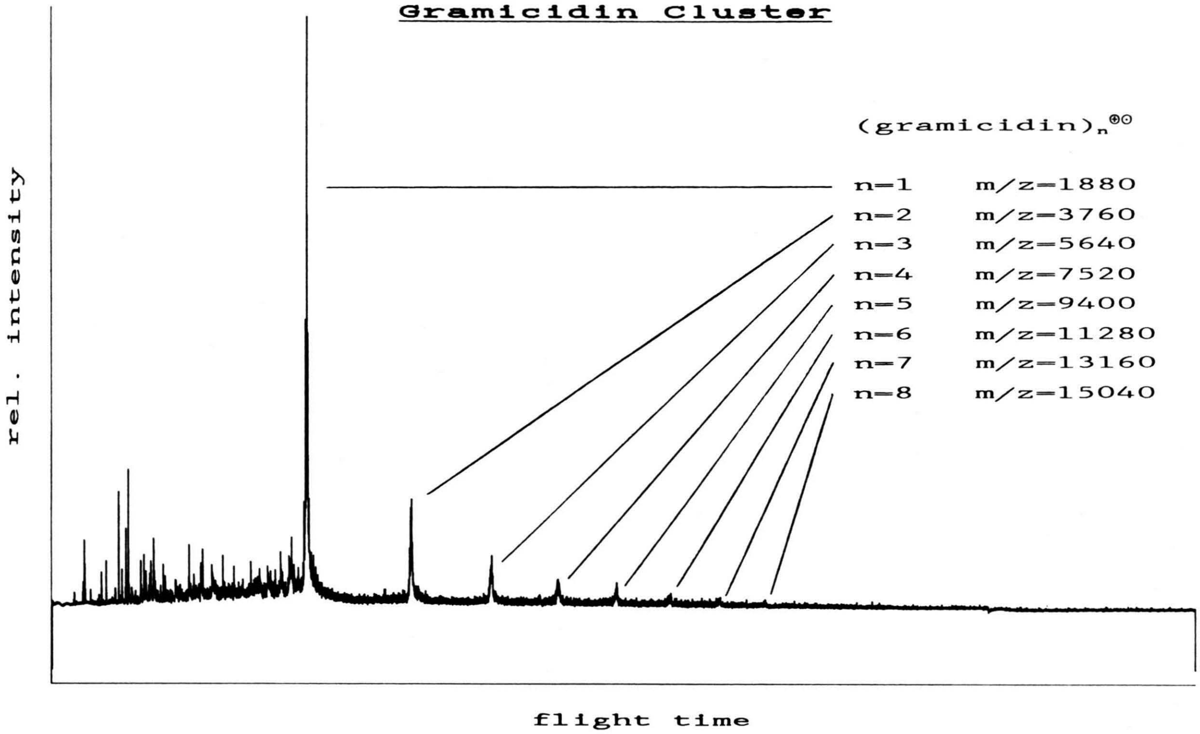


Fig. 7. Mass spectra of gramicidin obtained out of a solution in methanol (100 bar, 115 °C) with additional CO_2-laser desorption.

spectral resolution. Comparison between a computer simulation [8] of the absorption band with a rotational temperature of about 20 K simulation and experimental data indicate a rotational temperature of approximately 20 K at 220 °C and 25 K at 290 °C. These values correspond to a spectral resolution of about $0.5\ \mathrm{cm}^{-1}$.

A further example of the quality of the valve is shown in Figure 4a. Here the mass selected absorption spectrum of 1,3-dihydroxybenzene in the wavelength region from 276.0 to 279.0 nm is recorded. It is well known that this sample has four conformers, two of which are identical, which give rise to separated signals. Dunn et al. [9] have given some alternative assignments for the origin of the three bands however these assignments are not certain. One interpretation of the splitting of the band at 278.1 nm is due to the rotational features of the spectrum at low, free jet temperatures. We also observe splitting of this band which lends support to this valve design being able to produce low rovibrational temperatures. For gas phase measurements the valve allows an acquisition of high quality absorption spectra with respect to resolution and the high signal to noise ratio.

b) Liquids

It is well known from literature [5] that the cooling effect works best with a supersonic expansion of a monoatomic gas. In cases of liquids other mechanisms take place during the expansion [10]. Therefore the spectroscopic cooling effect as well as the spectral resolution drop dramatically.

This fact is illustrated by the Figs. 3 and 4. Here the sample, either benzene or 1,3-dihydroxybenzene, is mixed with a pressurized eluent, methanol, and then expanded into the vacuum. From Fig. 3c it is evident that the benzene molecules are less efficiently cooled [11]. The smearing of the sharp P-branch in the absorption spectra obtained at lower backing pressure is a good indication for the temperature of the benzene molecules. By comparison with computer simulation the rotational temperature of the benzene molecules can be estimated at about 100 K. The same behavior is seen in Fig. 4b for 1,3-dihydroxybenzene. The injection of this sample in methanol at a pressure of 200 bar at a nozzle temperature of 100 °C shows a decrease in the spectral resolution as well as a decrease in the signal to noise ratio. It should be noted that these effects are due to the cooling procedure of the liquid but not to the operation of the valve.

Despite the limited spectroscopic cooling the valve can certainly still be used for coupling chromatographic techniques to a TOF-MS. To demonstrate the principle a solution of about 2 µl benzene, 2 µl p-xylene and 2 µg fluorene in 50 µl methanol was separated by a 15 cm long packed C_{18} (7 µm) LC column (Macherey & Nagel) at 100 bar methanol backing pressure, 120 °C nozzle temperature and 0.8 ml/min flow rate. A part of the solution was injected into the mass spectrometer and ionized at a wavelength of 259 nm. Figure 5 demonstrates the successful separation and monitoring of the mass ranges 78 ± 0.3 amu (benzene), 106 ± 0.3 amu (p-xylene) and 166 ± 0.3 amu (fluorene). Clearly all substances are separated and can be detected 222 s, 245 s and 281 s after injection with a mean signal width of 20 s.

As described earlier, the direct introduction of nonvolatile molecules into the gas phase from a solution is restricted or impossible as a consequence of molecular aggregation. The aggregation results in a precipitation of the dissolved nonvolatile molecules shortly after the solution is injected into the vacuum. Therefore the valve nozzle has been surrounded by a U-shaped tube to collect the molecules. After deposition the molecule evaporation is performed by a CO_2-laser beam, In Figs. 6 and 7 are shown the mass spectra (obtained with a ionization wavelength of 270 nm) of tryptophan and gramicidin dissolved in methanol or water at a pressure of 100 bar and a nozzle temperature of 115 °C. By variation of the delay time between the UV-laser and the CO_2-laser pulse relative to the valve opening it is possible to create different mass spectra of tryptophan-methanol, tryptophan-tryptophan or tryptophan-water clusters. One example is shown in Fig. 6a, where the mass spectrum of tryptophan-methanol clusters is presented. A second example shows the mass spectra of tryptophan-tryptophan clusters up to four tryptophan units and the corresponding water clusters (Figure 6a). In the gramicidin spectrum clusters with a maximum size of eight units (m/z 15040) can be detected (Fig. 7), emphasizing the unlimited mass range and sensitivity of the valve assembly in combination with a TOF-MS.

These measurements illustrate the versatility of the designed interface and, when combined with additional laser desorption, the abundant opportunities for chromatographic introduction and investigation of nonvolatile molecules.

III. Conclusion

In summary, the novel pulsed valve design permits the use of mobile phases (gaseous and liquid) at low pressures (< 10 bar) up to temperatures of 350 °C and at higher pressures (300 bar) up to temperatures of 200 °C, to be introduced into pulsed working mass spectrometers, such as TOF or FT-ICR instruments. Minimization of dead volume and mobile phase splitting allows the described interface to be a versatile system for coupling chromatographic techniques to mass spectrometry. As a consequence of aggregation of nonvolatile molecules shortly after introduction into the vacuum, additional CO_2-laser desorption is employed for mass spectrometric measurements of biomolecules.

Acknowledgement

We gratefully acknowledge support of this work by the Bruker-Franzen GmbH (Bremen) and the Bundesministerium für Forschung und Technologie (13 N 5307); as well as the Deutsche Forschungsgemeinschaft (GR 917-1/2). The authors thank Dr. G. R. Kinsel for critical reading of the manuscript.

[1] J. Grotemeyer, J. Lindner, C. Köster, and E. W.. Schlag, J. Molec. Struct. **217,** 51 (1990).

[2] U. Boesl, H. J. Neusser, and E. W. Schlag, Chem. Phys. Lett. **61,** 57 (1979).

[3] T. Imasaka, T. Okamura, and N. Ishibashi, Anal. Chem. **58,** 2152 (1986).

[4] G. Rhodes, R. B. Opsal, J. T. Meek, and J. P., Reilly, Annal. Chem. **55,** 280 (1983).

[5] W. E. Henke, Dissertation at the Inst. Phys. Theor. Chem., TU München 1983.

[6] J. Grotemeyer, U. Boesl, K. Walter, and E. W. Schlag, Org. Mass Spec. **21,** 595 (1986).

[7] At high pressures and high temperatures graphite/vespel ferrules have better stabilities than pure graphite ferrules.

[8] K. Walter, Diploma thesis at the Inst. Phys. Theor. Chem., TU München 1985.

[9] T. M. Dunn, R. Tembreull, and D. M. Lubman, Chem. Phys. Lett. **121,** 453 (1985).

[10] B. N. Hale and P. L. M. Plummer, J. Atmos. Sci. **31,** 1615 (1974).

[11] The benzene is injected into methanol at a pressure of about 100 bar. The nozzle temperature was adjusted to 115 °C.