

# Single Photon Ionization (SPI) via Incoherent VUV-Excimer Light: Robust and Compact Time-of-Flight Mass Spectrometer for On-Line, Real-Time Process Gas Analysis

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**Fast on-line detection of organic compounds from complex mixtures, such as industrial process gas streams, require selective and sensitive analytical methods. One feasible approach for this purpose is the use of mass spectrometry (MS) with a selective and soft (fragment-free) ionization technique, such as chemical ionization (CI) or photo ionization (PI). Single photon ionization (SPI) with vacuum ultraviolet (VUV) light is a particularly soft ionization technique, well-suited for detection of both aromatic and aliphatic species. Problematic, however, is the generation of the VUV light. In general, the vacuum ultraviolet (VUV) light sources for SPI-MS are based either on lasers (e.g., 118-nm radiation generated by frequency-tripling of the third harmonic of a Nd:YAG laser) or on conventional VUV lamps, such as deuterium lamps. Although the laser-based techniques are very sophisticated and expensive, the conventional lamps have serious drawbacks regarding their optical parameters, such as low-output power, low spectral power density, and broad emission bands. In this work, a novel excimer VUV light source, in which an electron beam is used to form rare gas excimer species, is used. The excimer VUV light source produces brilliant and intense VUV light. The novel VUV light source was coupled to a compact and mobile time-of-flight mass spectrometer (TOFMS). A special interface design, including optical (VUV optics) as well as electronic measures (e.g., pulsed ion extraction) was realized. The use of the excimer VUV lamp for SPI will allow the realization of very compact, rugged, and sensitive SPI-TOFMS devices, which preferably will be adapted for process analytical application or monitoring issues (e.g., chemical warfare detection). The excimer VUV-lamp technology delivers VUV light with a good beam quality and high-output power at low costs. Furthermore, it allows changing the emitted wavelength as well as the bandwidth of the excimer VUV lamp in the 100–200-nm region by changing the gas filling. Consequently, SPI-TOFMS with an excimer light source is a fast detection technique that can**

**be used for online monitoring, for example, in environmental studies or industrial manufacturing processes. In this paper, technology and characteristics of the new excimer light source, as well as the combination with the TOFMS, are presented. Furthermore, a first characterization of the SPI-TOFMS instrument, regarding analytical parameters such as detection limits and selectivity, is given. This includes a discussion of potential improvements that probably will be achievable within a future prototype generation. Finally, first applications of the system for on-line measurement of organic trace species in a complex gas mixture (here, motorcycle exhaust gas) are presented.**

The standard approach for the analysis of organic (trace) components from complex samples is the use of hyphenated instrumentation, which combines a separation method with spectrometric detection. Commonly used separation techniques are both gas chromatography (GC) and high performance liquid chromatography (HPLC), whereas mass spectrometry is the most versatile spectrometric detector. A general drawback of these hyphenated methods, however, is the time-consuming step of chromatographic separation. Furthermore, after sampling (e.g., by adsorptive trapping), the samples often require pretreatment (e.g., by extraction) procedures, such as wet chemical precleaning and separation procedures (cleanup). The latter mentioned procedures exclude these methods for direct real-time on-line monitoring applications.

Within some sections of analytical chemistry, such as in the field of process analytical chemistry, a fast on-line analysis method is required. Currently, process gas constituents, such as NO<sub>x</sub> and SO<sub>2</sub>, occurring in high concentrations are detected via sensors.

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However, no standard technique is available for the on-line analysis of organic compounds occurring at low concentrations in process gases.

In principle, mass spectrometric methods with direct inlet sampling systems are well-suited for on-line monitoring. The standard 70 eV electron impact ionization technique (EI), however, is not applicable for on-line analytical applications focusing on characterization of complex organic mixtures, because EI causes massive fragmentation of organic molecules during the ionization process. Thus, the resulting mass spectra are congested by overlapping molecular and fragment ion patterns of the respective components of the mixture. Furthermore, if trace compounds in a matrix of bulk components or very complex mixtures are to be analyzed, at least some ionization selectivity is required. Recently, several applications of MS combined with alternative ionization techniques that allow fragmentationless (soft) as well as (partly) selective ionization for monitoring of complex mixtures of organic trace compounds have been reported. In particular, chemical ionization techniques as well as laser ionization methods were applied. Reported applications include real-time on-line monitoring results on automotive exhausts<sup>1-3</sup> and industrial process gases<sup>4-8</sup> as well as environmental applications.<sup>9,10</sup> The chemical ionization techniques used for on-line monitoring are, for example, positive chemical ionization by proton-transfer reactions (PTR)<sup>10</sup> and atmospheric chemical ionization in the negative ionization mode.<sup>8</sup> Several applications of PTR for the monitoring of trace gases have been reported. A drawback of the chemical ionization method, however, is their rather high sensitivity to matrix effects; i.e., the chemical composition of the sampled analyte gas can influence the ionization efficiency of a specific target analyte. Thus, although the CI methods have been very successful in on-line monitoring of environmental parameters, their usefulness to process analysis is restricted.

An alternative to chemical ionization is selective and soft laser-based photo-ionization techniques. Laser photo ionization can be performed either in a multiphoton or single photon absorption/ionization step. Resonance-enhanced multiphoton ionization (REMPI) is extremely selective; single photon ionization with VUV photons (SPI) is of medium selectivity, comparable to many CI methods. The laser-based ionization methods REMPI and SPI use pulsed laser radiation and are, thus, preferably combined with time-of-flight mass spectrometry (TOFMS). Preliminary monitoring applications of REMPI-TOFMS (e.g., coffee brew headspace)

have recently been reported.<sup>11,12</sup> Further studies have shown that SPI-TOFMS can be applied to generate on-line overview mass spectra of the major volatile organic compounds in coffee powder headspace.<sup>3</sup> Details on REMPI<sup>5,13-16</sup> and SPI<sup>3,17-21</sup> methods are given in the literature. Briefly the REMPI method, as commonly applied for analytical purposes, uses intense pulsed (~10-ns pulse width) UV laser radiation for a one-photon resonant two-photon ionization-process. Because of the resonance absorption step, UV-spectroscopy is involved in the photo ionization process, adding a new dimension of "optical" selectivity. REMPI-TOFMS is particularly well-suited to detection of traces of aromatic compounds, but it is difficult to ionize most aliphatic compounds with REMPI. The SPI method uses a single VUV photon for soft photo ionization. The ionization selectivity of SPI is given by the ionization energy (IE) of the compounds and the VUV wavelength, that is, only those compounds that have an IE lower than the photon energy are ionized (see Figure 1b). The single photon ionization technique (SPI) is also capable of ionizing aliphatic compounds if the VUV wavelength is short enough and, thus, has a somewhat complementary selectivity profile with respect to REMPI. SPI-TOFMS gives a survey over the (volatile) organic contents of the sample and exhibits a rather broad field of potential applications, ranging from on-line monitoring in the chemical industry to environmental monitoring. SPI can be performed using VUV laser pulses, which are generated in a frequency tripling process in a gas cell (third harmonic generation, THG).<sup>22-24</sup> For example, 355-nm laser pulses (third harmonic frequency of Nd:YAG laser) can be readily converted into 118-nm (10.5 eV) light using a gas cell filled with xenon of a pressure of some millibars. A photon energy of 10.5 eV ionizes most organic species, making the SPI method universal. Common bulk components, however, such as oxygen, nitrogen, carbon dioxide, or water are excluded from ionization. SPI is a very soft ionization method it is also well-suited for on-line applications, as recently demonstrated. For example, laser-based SPI-MS was applied to monitor automotive exhausts<sup>2,3</sup> and waste incineration flue gases.<sup>3</sup> Furthermore the headspace analysis of complex mixtures, such as gasoline and coffee powder, was reported.<sup>3</sup>

The major drawback of laser-based photo ionization techniques REMPI and laser-based SPI is the need to use expensive bulky and sophisticated laser systems. Nonlinear optical processes are

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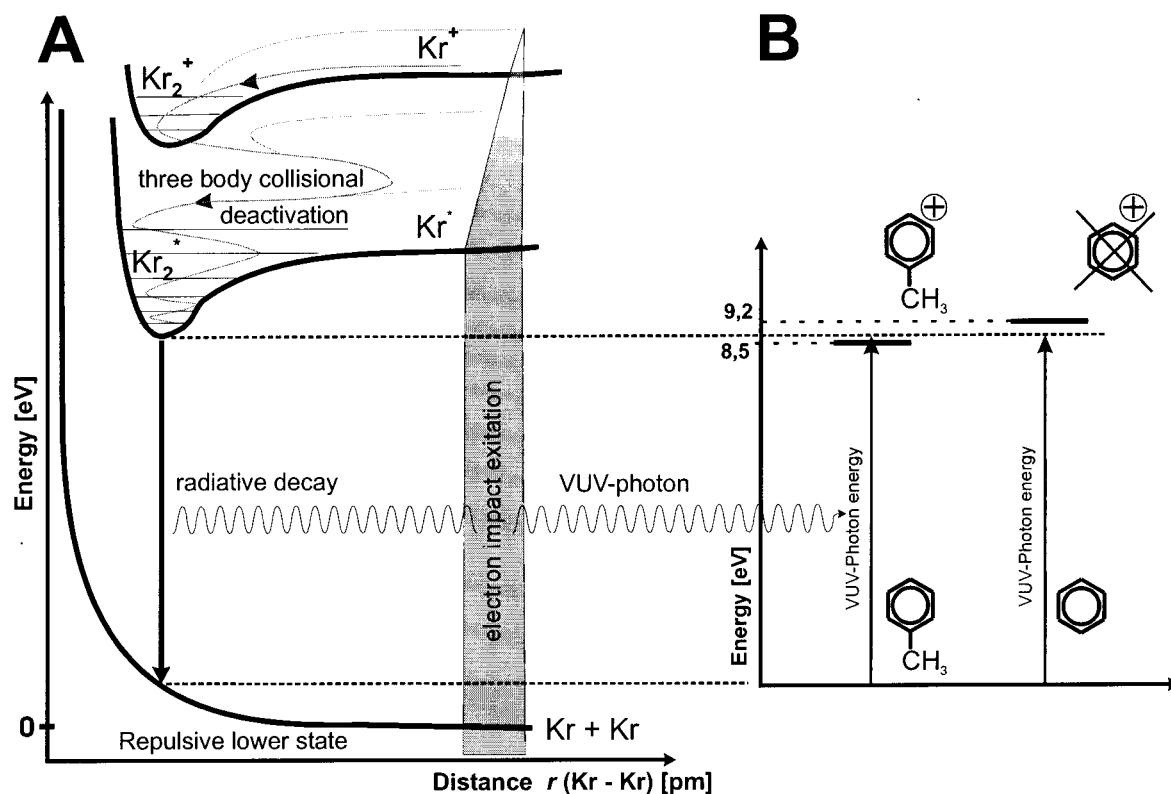


Figure 1. (A) Schematic representation of VUV photon generation by radiative dissociation of rare gas excimers. (B) Schematic drawing of the single photon ionization (SPI) process using VUV-excimer photons.

involved either in the ionization process (i.e., the two-photon ionization process in REMPI) or the generation of the ionization laser pulses (i.e., the frequency-tripling process for generating VUV photons for SPI). Because of this nonlinear process, the final output signal,  $s$  (i.e., ion current), is proportional to the primary laser pulse intensity,  $I$ , as described by the equation,  $s \sim I^n$ , where  $n$  is at least 2. Furthermore, other laser beam parameters, such as beam profile quality, divergence, or coherence, have a strong influence on the output signal. Therefore, careful control of the laser parameters is crucial for quantitative measurements.

In principle, single photon ionization mass spectrometry can also be performed using VUV lamps, for example, deuterium lamps, as the photon source. Their power density, however, is weak in the spectral range in question. This excludes MS with conventional VUV-lamp ionization from applications considering fast on-line analysis of trace compounds.

In this work, a new nonlaser VUV photon source, namely an electron-beam-pumped rare gas excimer lamp, was applied as a SPI source for mass spectrometry. In detail, an interface between a prototype of the novel VUV lamp and a compact, mobile time-of-flight mass analyzer was realized. With this novel VUV lamp, it is possible to generate relatively monochromatic, intense, and brilliant VUV radiation. By exchanging the rare gas mixtures in the lamp, different wavelengths can be generated.

Results obtained with the new VUV-excimer-lamp time-of-flight mass spectrometer are presented. These include laboratory measurements of headspace gases of volatile chemicals and on-line measurements of organic compounds in the exhaust gas of a motorcycle engine.

## INSTRUMENTATION AND EXPERIMENTAL SETUP

**(A) The Electron-Beam-Pumped Excimer VUV Lamp.** In principle, various types of VUV light sources can be considered as photon source for SPI photo-ionization. A common vacuum ultraviolet light source is the deuterium discharge lamp. The vacuum ultraviolet spectrum of deuterium consists of a weak broad-band continuum; the Werner and Lyman molecular bands around 130 and 160 nm, respectively; and the narrow Lyman  $\alpha$  atomic line at 121.567 nm. The broad continuum emission profile of deuterium lamps and the rather low spectral energy are disadvantageous for their use as SPI-VUV light sources for analytical mass spectrometry.

Over the past 10 years, other more efficient types of VUV lamps based on rare-gas excimer emission have been developed. Excimers are molecules that are bound only in an excited electronic state (i.e., electronic deactivation of the excimers leads to their dissociation). Diatomic excimer molecules are known for all rare gases. Radiative decays of Ar<sub>2</sub><sup>\*</sup> and Kr<sub>2</sub><sup>\*</sup> to the repulsive ground state of the two rare gas atoms have been used as the light-emitting process in the experiments described here. The central wavelengths of the emission bands are at 126 nm for Ar<sub>2</sub><sup>\*</sup> and 147 nm for Kr<sub>2</sub><sup>\*</sup> (see Table 1). The emission is due to the second excimer continua, which correspond to the decay of fully vibrationally relaxed excimer molecules, have a spectral bandwidth of typically 10 nm, and dominate the emission spectra for gas pressures typically above 100 mbar. Excimer emission from rare gases was described as early as 1958 by Tanaka.<sup>25</sup> Figure 1A shows a schematic representation of the excimer-emission pro-

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Table 1. Excited Species, Emission Process, Center Wavelengths, Photon Energy at Center Wavelength, Relative Photon Output and Emission Band-Width of Different Rare Gases and Gas Mixtures

gas or gas mixture	excited species	emission process	center wavelength nm	photon energy at center wavelength eV	estimated conversion rate <sup>a</sup> %	bandwidth nm
He	He <sub>2</sub> <sup>*</sup>	radiative excimer decay	60/80	20.7/15.5	~40	20
Ne	Ne <sub>2</sub> <sup>*</sup>	radiative excimer decay	83	14.9	~40	4.5
Ar	Ar <sub>2</sub> <sup>*</sup>	radiative excimer decay	126	9.8	~40	9
Kr	Kr <sub>2</sub> <sup>*</sup>	radiative excimer decay	147	8.4	~40	11
Xe	Xe <sub>2</sub> <sup>*</sup>	radiative excimer decay	172	7.2	~40	14
Ne/H <sub>2</sub>	H <sup>*</sup>	atomic emission line (after energy transfer)	121.57	10.20	~10	<0.1
Ar/Xe Kr/Xe	Xe <sup>*</sup>	atomic emission line (after energy transfer)	147	8.4	~10	<0.1
Ar/O <sub>2</sub>	O <sup>*</sup>	atomic emission line (after energy transfer)	130	9.5	~10	<0.1
Ne/Ar/Kr	Kr <sup>*</sup>	atomic emission line (after energy transfer)	124	10.0	~10	<0.1
Ar/F <sub>2</sub> Ne/F <sub>2</sub>	F <sub>2</sub> <sup>*</sup>	radiative excimer decay	157	7.9	~10	2
Ar/F <sub>2</sub>	ArF <sup>*</sup>	radiative excimer decay	193	6.4	~10	2

<sup>a</sup> Percentage of the electron energy deposited in the rare gas that is converted into VUV radiation.

cess. Excimer molecules form in three body collisions from the energetically high-lying excited levels of rare gas atoms ( $\approx 11.8$ , 10.0, and 8.4 eV in Ar, Kr, and Xe, respectively).<sup>26</sup> Therefore, the rare gas atoms have to be excited to high electronic levels in cold dense gases in which molecules can be readily formed. Practical use of the highly efficient excimer emission, however, has been delayed until appropriate excitation methods for effective excimer-molecule formation were found.

One known rare gas excimer VUV light source is the barrier discharge lamp.<sup>27</sup> Excitation to high levels is achieved in intense discharges that are distributed in space and time, and molecule formation occurs in the afterglow of these discharges. This process, however, fails to provide the brilliant VUV sources required for the applications described here. Another alternative way for rare gas excimer formation is the microhollow cathode discharge in which a glow discharge can be operated at high density by confining the discharge current to narrow channels in a dielectric material.<sup>28</sup> A disadvantage of these lamps is the erosion of the electrodes, leading to impurities and, consequently, to a poor quality of the emitted spectrum and to changes of the spectrum.

In this paper, a new type of excimer light source has been used in which excimer molecules are formed via electron beam excitation of dense rare gases.<sup>29</sup> A schematic view of the light source connected to a time-of-flight mass spectrometer (TOFMS) is shown in Figure 2A. Briefly, a 10–20 keV electron beam is formed using a regular electron source of the same type as used in monochrome TV tubes. The main innovation of the light source is an extremely thin ceramic foil through which relatively slow electrons can be sent into dense gases with only 5–10% energy loss. The  $1 \times 1$  mm<sup>2</sup> foil, made of silicon nitride (SiN), is only 300 nm thick. Since the foil is completely vacuum-tight and highly temperature-resistant, with a melting point of 1900 °C, it is an ideal material to decouple the vacuum, in which the electron beam is

formed and accelerated from the dense gas where the excimer molecules are produced. For practical applications, electron-beam-induced excimer formation had been previously used only in large electron-beam-pumped laser devices. Using thin ceramic foils as entrance windows instead metal foils, which have to be typically 10 times thicker in order to be completely vacuum-tight, leads to the compact brilliant VUV-excimer light source shown in Figure 2B. The electron-beam-induced excimer light source has the advantage that the rare gas parameters do not depend on the excitation, in contrast to discharge excitation in which certain ignition and burning conditions always have to be met. In addition, high gas purity, which is an important issue for efficient excimer light emission, can easily be achieved and maintained using this electrodeless excitation method. This leads to the clean excimer spectra shown in Figure 3. The low electron energy, which is possible when using the thin entrance foils, leads to very favorable conditions for building brilliant light sources. Conversion efficiencies from electron beam power into VUV light on the order of 40% have been measured<sup>29</sup> and efficiencies up to 60% are predicted for optimized operating conditions by a theoretical model.<sup>30</sup> Thus, for a continuously (cw) operated VUV lamp with an electron beam power of 1 W, a flux of  $3 \times 10^{17}$  photons/s (Kr<sub>2</sub><sup>\*</sup> excimer, 147 nm) is generated. The penetration depth of an electron of 10 keV kinetic energy in the heavier rare gases (Ar, Kr) at atmospheric pressure is on the order of only  $\sim 1$  mm. This low penetration depth leads to a small, bright, almost spherical VUV-light-emitting volume right in front of the foil through which the electron beam enters the rare gas chamber. The power density in the gas is proportional to the electron energy  $E$  by  $E^{-4.25}$  for a fixed electron beam current. The light source can be operated from fully continuous to short pulsed by using a continuous or pulsed electron beam.<sup>31</sup> The bottleneck for increasing the emitted light intensity lies in the thermal destruction threshold of the ceramic entrance foil, because the thermal stress applied to the entrance foil is proportional to the average electron flux. Higher light

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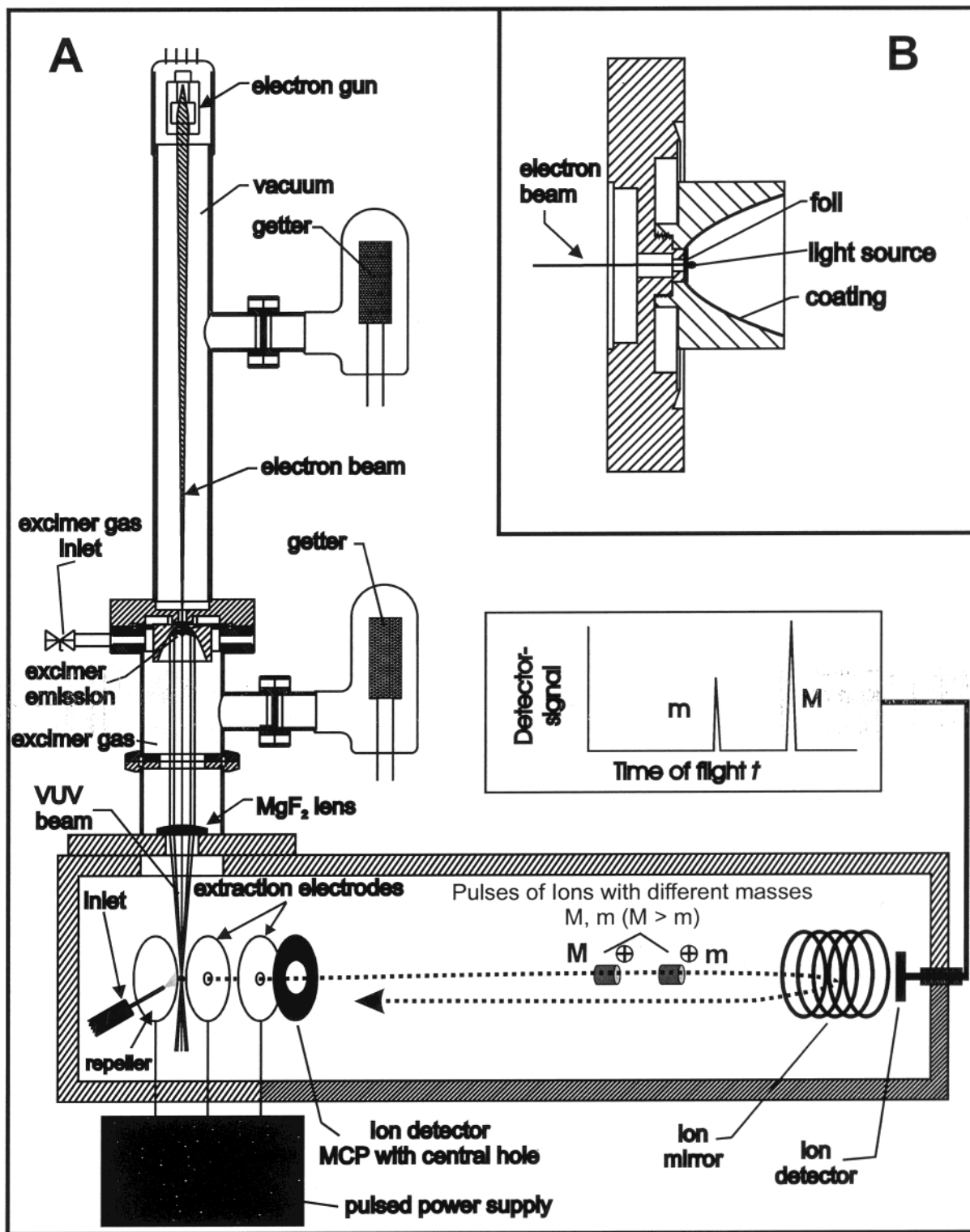


Figure 2. (A) Schematic drawing of the electron-pumped excimer light source connected to a time-of-flight mass spectrometer for single photon ionization. (B) Expansion of the zone where the light is produced at a well-defined spot close to the electron beam entrance window (i.e., a 300-nm-thick SiN foil).

intensities can be obtained in the pulsed mode. The minimum pulse width is given by the excimer kinetics and is on the order of several hundreds of nanoseconds for Ar and Kr at typically 1 bar. The pulsing mode was used in most of the experiments described here in order to achieve maximum VUV light intensities. The ions were then extracted at the end of the light pulses. For

the experiments described below, the light source was operated at a repetition rate of 120 Hz with an electron beam current of typically 1 mA during the pulses corresponding to  $\sim 10$  W electron beam power and 4 W VUV light output during the pulses. Different rare gas fillings could be used in the light source (Figure 3). Relative intensities and the pulse shape of the light pulses could

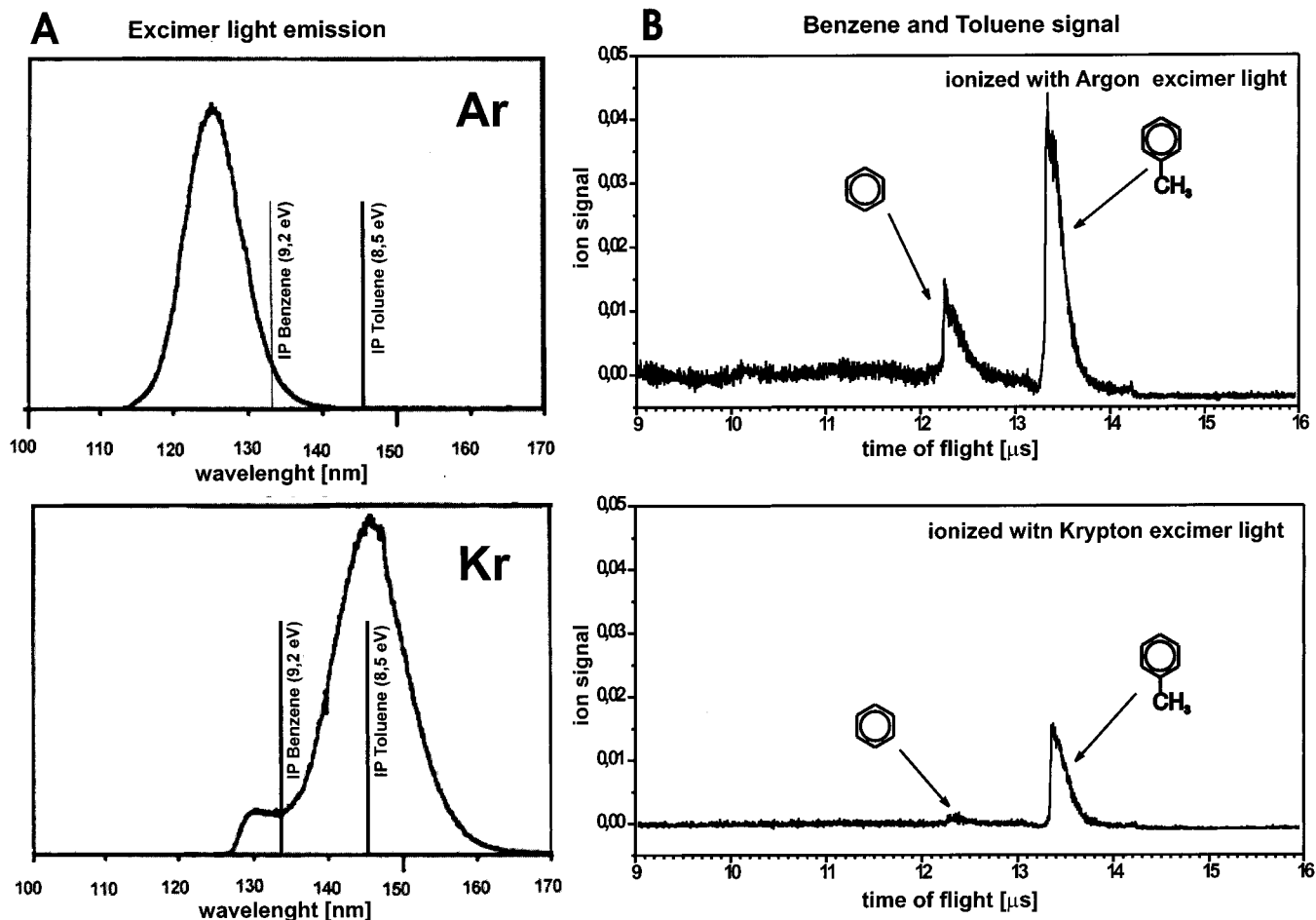


Figure 3. (A) Excimer emission spectra of argon ( $\text{Ar}_2^*$ , top) and krypton ( $\text{Kr}_2^*$ , bottom). The ionization potentials of benzene and toluene are indicated. (B) Electron-pumped excimer-lamp SPI TOFMS mass spectra of benzene and toluene recorded with excimer light from argon ( $\text{Ar}_2^*$ ,  $\lambda_{\text{cent.}} = 126 \text{ nm}$ , top) and krypton ( $\text{Kr}_2^*$ ,  $\lambda_{\text{cent.}} = 147 \text{ nm}$ , bottom). With krypton ( $\text{Kr}_2^*$ , 147 nm, bottom), a selective ionization of toluene is feasible.

be measured by using a VUV-sensitive solid state detector next to the gas sample in the ion source. The light-producing rare gases were circulated by a metal bellows compressor through the light source and an external (800 °C) titanium rare gas purifier. A fixed gas filling and a small getter pump<sup>32</sup> would be used in a technical realization of the analytical device described here. Such a getter pump from SAES getters is already being used to maintain the vacuum in the electron beam tube (Figure 2A). Light emission processes and achievable UV/VUV wavelengths that can be produced by the light source are listed in Table 1.

**(B) Time-of-Flight Mass Spectrometer.** A compact linear in-line reflectron time-of-flight mass spectrometer with a field-free drift region of 634 mm, equipped with an ion source originally designed for laser ionization was used for the experiments reported here.<sup>3</sup> The inlet cell and the flight tube of the TOFMS are differentially pumped by 210 L/s and 60 L/s turbo molecular pumps, respectively. The Wiley–McLaren-type ion source<sup>33</sup> can be operated with static or pulsed acceleration fields. The repeller electrode and the first extraction electrode have the same potential with opposite polarity to ensure ground potential for the central ionization region (i.e., to minimize field disturbances from the

sample inlet needle), as described for a preceding instrument in ref 5. The field-free drift region is on the same negative potential as the second extraction plate. After the second extraction electrode, the ion beam passes an electrostatic lens unit as well as an  $x$ – $y$  deflection plate unit for controlling the ion trajectories. The ions enter the field-free drift region through a small tube, leading through the central hole of the 1.57-in. dual channel plate detector. A second detector is mounted behind the ion mirror for operation of the mass spectrometer as a linear TOFMS<sup>33</sup> (i.e., by deactivating the ion mirror potential). In the linear mode, the field-free drift region is 430 mm. The operation as linear TOFMS allows an increased sensitivity as a result of enhanced transmission.

The applied “needle” sample inlet technique has been previously described in detail.<sup>5,34</sup> Briefly, a stainless steel needle reaches into the center of the ion source. Within the steel needle runs a deactivated fused-silica capillary (i.d., 0.32 mm). An effusive molecular beam is formed at the open end of the capillary. The molecular beam is ionized ~2 mm below the end of the capillary. Sampling was performed via a 1-m fused-silica capillary. For the preliminary study presented here, neither the inlet system nor the sampling capillary was heated. For addressing higher molec-

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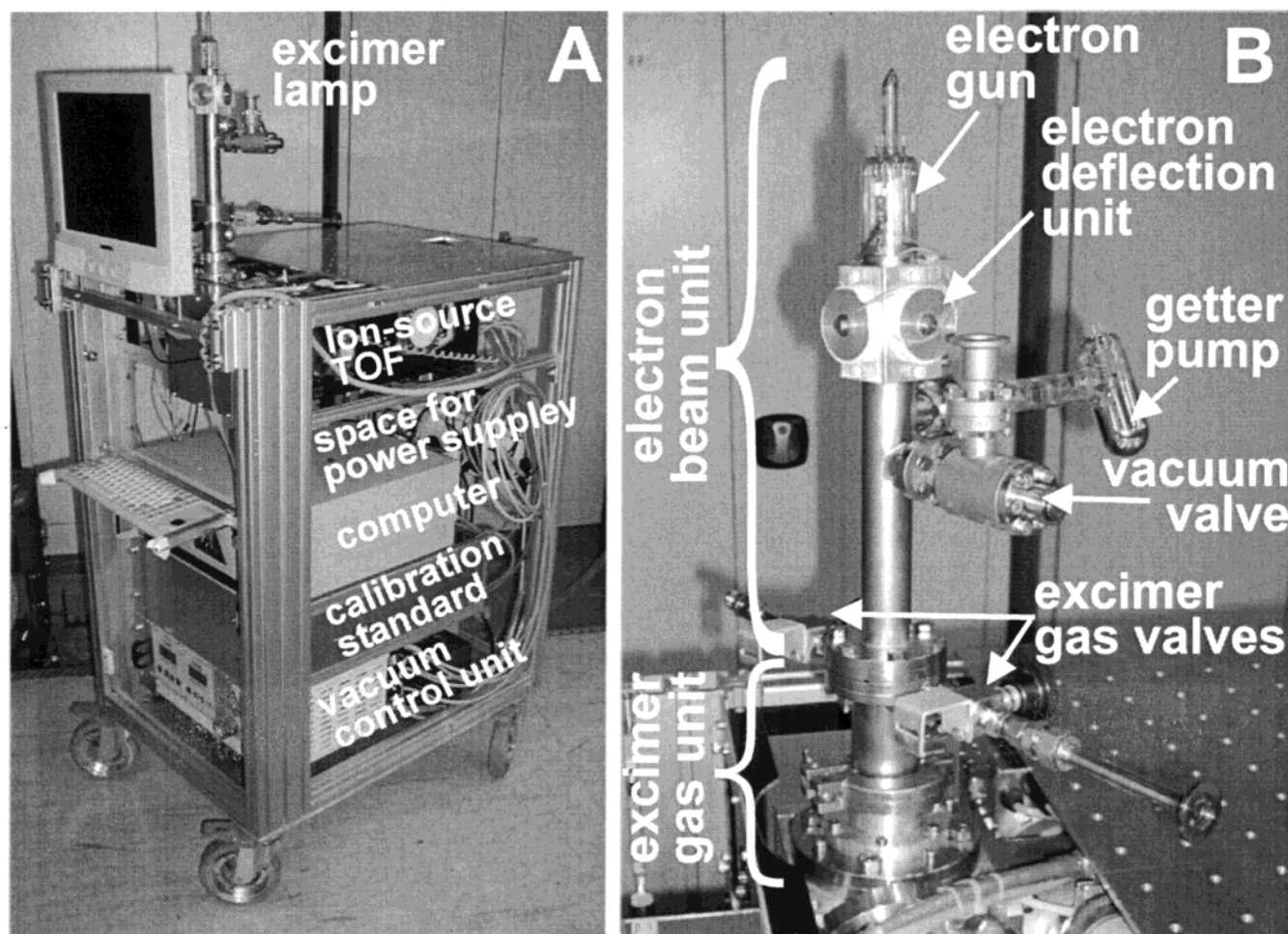


Figure 4. (A) Photograph of the 19-in. mobile TOFMS system with the electron-beam-pumped excimer light source. (B) Close-up photograph of the electron-beam-pumped excimer lamp.

ular weight compounds, heated inlet and sampling systems, as described previously,<sup>5,34</sup> will be applied. The sampling gas flow through the capillary was  $\sim 10$  mL/min (standard conditions). Data acquisition was performed either via a 250 MHz 1 GS/s transient recorder PC card (acqiris, Switzerland) or by a digital oscilloscope (Le Croy, type LT344). Details on the external calibration procedure for generating quantitative data and the determination of detection limits are also available in the literature.<sup>3,5</sup>

**(C) Coupling of the Excimer VUV Lamp and the TOF Mass Spectrometer.** In this work, a previously built TOFMS system, which was designed for laser ionization methods, was coupled to a laboratory prototype of an electron-beam-pumped rare gas excimer VUV lamp. A special flange was designed to interface the excimer light source and the TOFMS system. An optical system was designed to direct the VUV light from the excimer light source onto the molecular beam in the center of the TOFMS ion source. The optical elements of the imaging system were placed in the rare gas volume. A parabolic aluminum mirror coated with a  $\text{MgF}_2$  protective layer was used to collect and direct the VUV radiation formed in the active volume near the SiN foil. The second part of the optical system was a VUV-transmitting  $\text{MgF}_2$  plano-convex lens with a focal distance of 79 mm at 121 nm. The  $\text{MgF}_2$  lens focused the direct VUV light onto the molecular beam in the center of the TOFMS ion source. This  $\text{MgF}_2$  lens was also

used to seal the rare gas volume against the vacuum in the ion source. The optical system is shown in Figure 2.

In earlier applications, the TOFMS unit was used for laser ionization experiments (REMPI, SPI) using pulsed (5-ns duration) laser radiation in combination with a static extraction field. The VUV lamp emission cannot be pulsed as fast as a laser because of gas kinetic reasons. In the present setup, VUV light pulses of  $\sim 8\text{-}\mu\text{s}$  pulse width were generated (see Figure 5). To achieve appropriate starting conditions for the time-of-flight mass analysis, the HV for ion extraction was gated. The repeller and the extraction electrodes were pulsed by means of fast-triggerable HV switches (Behlke Electronic GmbH, Germany, push-pull switches type HTS 31-GSM with a rise time of 15 ns/3 kV). The HV-switches were placed a short distance from the ion-source's vacuum feed through connectors in order to reduce the emission of electromagnetic radiation. Nevertheless, because the internal connections to the acceleration plates in the ion source in the vacuum region are not HF-shielded, some signal is picked off by the multichannel plate detector (MCP), which is acting as an antenna for HF electromagnetic radiation. The noise of the detector signal (Figure 5, trace C) at  $12\text{ }\mu\text{s}$  is induced by the electromagnetic field of the extraction HV pulse.

The HV switches for the ion extraction as well as the electron beam of the VUV lamp were triggered by two delay generators



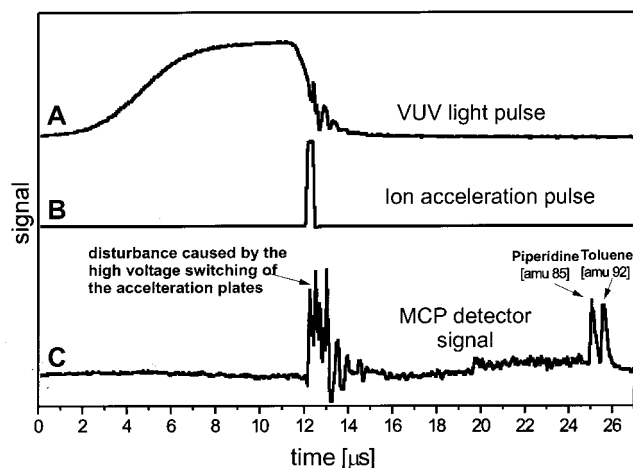


Figure 5. (A) VUV excimer light pulse as detected by a photo detector. (B) Trigger pulse for the fast push–pull switching of the high voltages for the repeller and extraction electrodes of the TOFMS ion source. (C) Signal output of the multichannel plate (MCP) detector of the TOFMS. The ion extraction HV pulse causes disturbances due to inductive effects. Later, the TOF ion signals of piperidine and toluene are visible.

(Stanford Research Instruments Inc., model DG535).

The timing of the processes is shown in Figure 5. The electron beam was gated by switching the extraction voltage of the electron gun. The cathode filament was operated continuously at typically 6 V and 20  $\mu$ A. At 12  $\mu$ s after enabling the electron beam extraction voltage, the electron beam was switched off and the HV switches were triggered. The HV was applied for 350 ns to accelerate the ions from the ionization zone into the TOFMS drift tube. The delay generators allowed to vary all trigger pulses to vary for conveniently optimizing the triggering scheme. Figure 5 shows the time-dependence of VUV light output (trace A) as detected with a VUV/XUV detector (IRD Inc., type AXUV-20), the trigger pulse for the TOFMS extraction HV pulse (trace B), and the TOFMS MCP detector signal (trace C). For this measurement, a gas sample containing piperidine and toluene was sampled. The ionized molecules were detected at 13 and 14  $\mu$ s (trace C), respectively, after the trigger for the ion extraction. The TOFMS was operated in the reflectron mode. Details of the delayed extraction pulse are as follows: During the VUV light pulse, the repeller and first extraction electrodes were maintained at ground potential. After triggering the delayed extraction (trace B), the repeller and extraction electrodes were pulsed to  $-400$  and  $+400$  V, respectively. All other voltages of the TOFMS were kept constant. In detail, the liner voltage (flight tube) and reflector entrance electrode were set to  $-2500$  V. The two connected electrodes in the double-stage ion mirror (which consists of 10 equidistant electrodes over a depth of 64 mm connected via a uniform resistor chain) were fixed at  $-500$  V (6th electrode) and  $+450$  V (reflector end plate, 10th electrode).

## RESULTS AND DISCUSSION

**(A) Characterization of the Method: Detection Limits, Fragmentation and Wavelength Selectivity.** The sensitivity of the instrument was tested with a calibration standard gas that contained 10 ppm (v/v) of benzene, toluene, and 1,4-xylene (BTX),

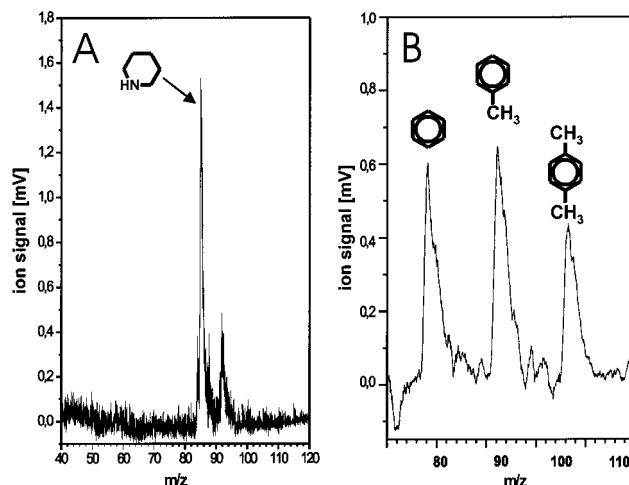


Figure 6. (A) Direct inlet mass spectrum of a piperidine sample recorded with the electron-beam-pumped excimer-lamp TOFMS ( $\text{Ar}_2^*$ ,  $\lambda_{\text{cent.}} = 126$  nm). See also Table 2. (B) Direct inlet mass spectrum of calibration standard gas containing 10 ppm (v/v) benzene, toluene, and xylene (BTX) in nitrogen, measured with electron-beam-pumped excimer-lamp TOFMS ( $\text{Ar}_2^*$ , 126 nm). See also Table 3.

in nitrogen (10 L, 200 bar steel cylinder, Messer Griessheim GmbH, Germany). Piperidine in air was used for determination of the degree of fragmentation. Sampling was performed by an unheated, deactivated fused-silica capillary. For the mass spectra shown, the excimer lamp and the ion source were pulsed according to the scheme shown in Figure 5 with a repetition rate of 120 Hz. A total of 500 single transients were averaged to form the mass spectrum shown.

In Figure 6A and B, the SPI-TOFMS mass spectra of a piperidine sample and the calibration gas mixture, respectively, are shown. The electron-beam-pumped excimer lamp was operated with a 450 mbar Ar rare gas filling ( $\text{Ar}_2^*$ ,  $\lambda_{\text{cent.}} = 126$  nm). No fragmentation was observed, even for the rather fragile piperidine molecule. The peak at 92  $m/z$  in the headspace mass spectrum of piperidine (85  $m/z$ ) is due to residual toluene from a previous measurement. Since the coupling of the VUV light source and the TOFMS is based on a preliminary concept and is by far not optimized, only a rather poor mass resolution was achieved ( $m/\Delta m_{50\% \text{ valley}} = 88$  at 85  $m/z$ ). Future work will address the optimization of the mass spectrometric performance of the method (see Discussion Section). In Table 2, mass spectrometry data from piperidine using EI ionization (75 eV)<sup>35</sup> and the described excimer light ionization technique are given. Although the piperidine mass spectrum is dominated by fragments (only prominent fragments with a relative intensity above 20% are considered), no fragmentation is recognizable using the SPI technique. The softness of the SPI method is very advantageous, enabling on-line analytical applications for complex gas mixtures.

In Figure 6B, the electron-beam-pumped excimer-lamp SPI-TOFMS mass spectrum ( $\text{Ar}_2^*$ ,  $\lambda_{\text{cent.}} = 126$  nm) of a calibration gas mixture containing benzene, toluene, and 1,4-xylene (BTX) with a concentration of 10 ppm (v/v) is shown. A total of 500 single transients were averaged for the mass spectrum. For determina-

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Table 2. Mass Spectral Data for Piperidine Recorded with Electron Pumped Excimer-Lamp TOFMS<sup>a</sup> and Electron Impact Ionization MS<sup>b,35</sup>

	mass peaks from piperidine, $m/z$						
	42	43	44	56	57	84	85 ( $M^+$ )
relative abundance for SPI ( $Ar_2^*$ , $\lambda_{cent.} = 126$ nm), %	0	0	0	0	0	0	100
relative abundance for EI (75 eV), %	25	22	33	44	44	100	53

<sup>a</sup> SPI,  $Ar_2^*$ ,  $\lambda_{cent.} = 126$  nm. <sup>b</sup> The relative abundance of prominent mass peaks (<20% rel abundance) is compared. In the case of the SPI spectrum, no fragmentation was detectable.

Table 3. Detection Limits for BTX compounds Achieved with the Electron-Pumped Excimer-Lamp TOFMS<sup>a</sup>

compd	S/N for the 10 ppm (v/v) standard	detection limit (S/N = 2), ppm (v/v)
benzene	10	2
toluene	9	2
1,4-xylene	7	3

<sup>a</sup>  $Ar_2^*$ ,  $\lambda_{cent.} = 126$  nm.

tion of the detection limit, the raw mass spectrum was smoothed (boxcar averaging over 0.25 mass units) in order to remove high-frequency electronic noise. Detection limits in the low parts-per-million (v/v) range were determined for the BTX compounds according to the method described in a previous work<sup>5</sup> and are listed in Table 3.

As shown in Figure 3A and Table 1, the UV/VUV emission wavelength depends on the rare gas in the gas chamber of the electron pumped excimer light source. In Figure 3, the emission spectra of argon and krypton excimer light are shown. Ionization potentials (IP) of benzene and toluene are also indicated in the graph. In Figure 3B, electron pumped rare gas excimer-lamp TOFMS mass spectra of an on-line sampled mixture of benzene and toluene are depicted. The upper trace was recorded using ionization with Ar excimer light ( $Ar_2^*$ ,  $\lambda_{cent.} = 126$  nm) and the lower trace, using ionization with Kr excimer light ( $Kr_2^*$ ,  $\lambda_{cent.} = 147$  nm). The energy situation in the latter case ( $Kr_2^*$ ,  $\lambda_{cent.} = 147$  nm) is schematically depicted also in Figure 1B. With the light emitted from the Kr excimer (center wavelength 8.4 eV with a fwhm of 0.7 eV), ionization of toluene (IP = 8.8 eV) is possible, but the ionization of benzene (IP = 9.2 eV) is suppressed (lower trace in Figure 3B). Ar excimer light (center wavelength 9.8 eV with a fwhm of 0.7 eV), on the other hand, readily ionizes both species (upper trace in Figure 3B). The ionization selectivity can be useful to discriminate between isobaric molecules in complex samples or to suppress bulk compounds with high IP (e.g., oxygen, water, and nitrogen). By using different rare gases or gas mixtures from Table 1, a large variety of different wavelengths and bandwidths is available for specific analytical applications.

**(B) Application Example: On-Line Real Time Measurement of Organic Compounds in the Exhaust Gas of a Motorcycle.** The scope of the novel VUV lamp TOF mass spectrometer lies clearly in the field of on-line monitoring applications for industrial process analysis (e.g., mineral oil processing) and product control (e.g., food quality via headspace analysis). Furthermore, on-line applications in the field of envi-

ronmental monitoring, detection of chemical warfare agents, scientific studies, and medical diagnosis are conceivable. To demonstrate the potential of the method, an on-line analysis of exhaust gas from a motorcycle (Yamaha, Japan, model 43F) was performed. Exhaust gas was sampled via a deactivated fused-silica capillary from the motorcycle's exhaust pipe.

In Figure 7A, a mass spectrum of on-line sampled motorcycle exhaust gas (averaged from 60 single transients) acquired shortly after starting the engine is shown ( $Ar_2^*$  excimer,  $\lambda_{cent.} = 126$  nm). Although the mass resolution of the prototype instrumentation is still rather limited, the series of alkylated benzene derivatives, namely, benzene (78  $m/z$ ), toluene (92  $m/z$ ), xylenes, and ethylbenzene (106  $m/z$ ) and trimethylbenzene (120  $m/z$ ), can readily be identified. Other mass peaks were observed at 70 and 84  $m/z$ , which probably are due to the prominent internal combustion engine exhaust gas compounds crotonaldehyde and pentenal. In Figure 7B, a continuous on-line measurement sequence is depicted. The upper part of Figure 7B shows a 3D contour plot of the MS data acquired over a time span of 125 s. The data set used for this 3D representation consists of 110 data files, each containing the data for a single spectrum averaged from 60 single spectra at 120 Hz. The procedure for composing the 3D plots is based on a custom-written (LabView, programming environment) software package, as reported in previous REMPI-TOFMS applications.<sup>5</sup> Although the sampling system was not heated, the monitored compounds show highly dynamic behavior during the short accelerating phases. Whereas the  $x$  and  $y$  axes are representing the time [s] and the molecular mass [ $m/z$ ] (50–140  $m/z$ ), the gray scale coding is according to the ion signal intensity. Traces of alkylated benzene derivatives (78, 92, 106, and 120  $m/z$ ) are clearly visible. Three short cycles, that is, engine start, idle run (partly with some rapid accelerations), and engine stop, are indicated in the contour plot. The medium cycle is also represented expanded as a 3D landscape plot (Figure 7B, bottom). Here, the sharp emission maxima of aromatic compounds during short acceleration phases are revealed.

In Figure 8, finally, four time-vs-intensity profiles from the motorcycle exhaust gas measurements are given. The profiles of benzene (78  $m/z$ ), toluene (92  $m/z$ ), xylenes/ethylbenzene (106  $m/z$ ), and the  $C_3$ -alkylated benzene derivatives (120  $m/z$ ), extracted from the 3D landscape plot in Figure 7B, are given in detail. The traces of benzene and toluene were quantified by external calibration (i.e., according to the system response to a calibration gas standard; see Figure 6B). A tentative calibration of the 106  $m/z$  trace is given (sum of  $C_2$ -alkylated benzene derivatives) using the calibration gas standard signal for 1,4-xylene. This approach is possible because the SPI response for closely

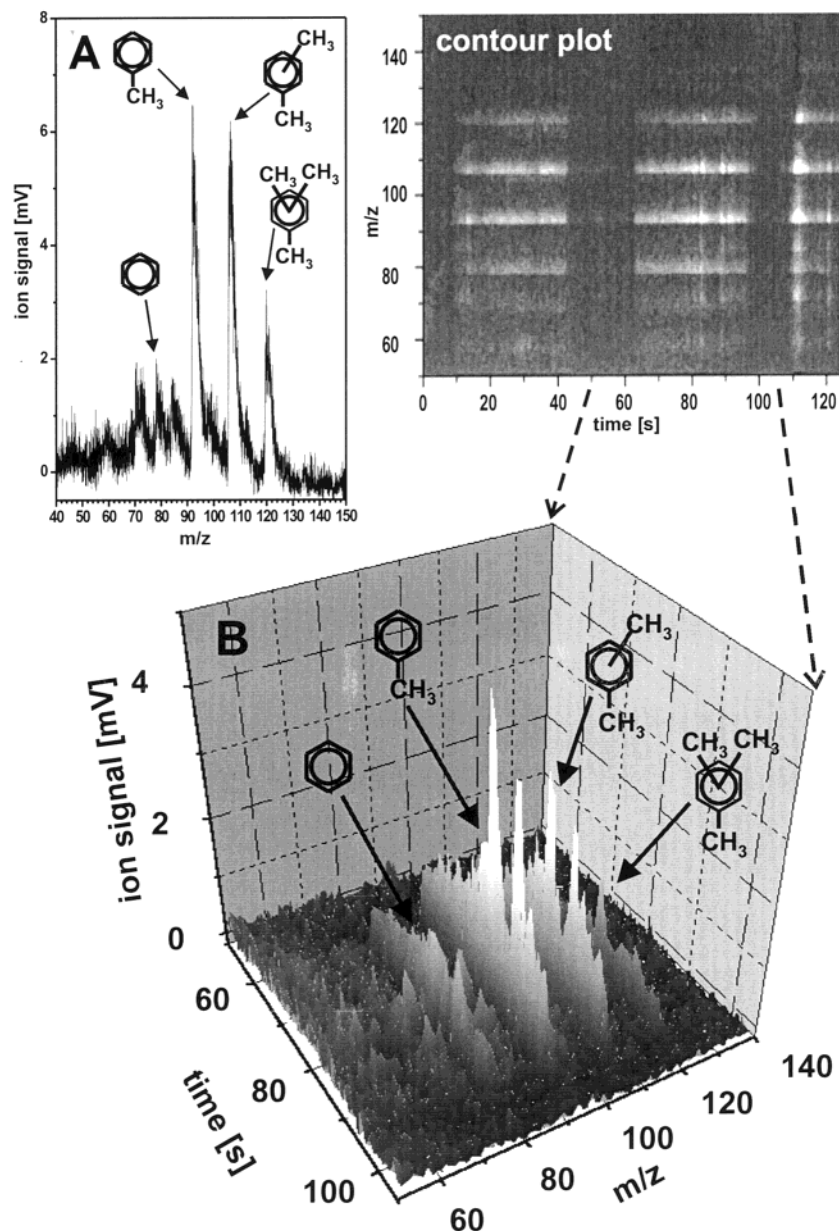


Figure 7. (A) Direct inlet mass spectrum of on-line sampled exhaust gas from a motor bike measured shortly after the engine's start by electron-beam-pumped excimer-lamp TOFMS ( $\text{Ar}_2^*$ ,  $\lambda_{\text{cent.}} = 126 \text{ nm}$ ). (B) 3D presentation of a continuous on-line measurement of the exhaust gas of a motorcycle with electron-beam-pumped excimer-lamp TOFMS ( $\text{Ar}_2^*$ ,  $\lambda_{\text{cent.}} = 126 \text{ nm}$ ). The emission behavior of monocyclic aromatic compounds (benzene, toluene, xylene—BTX) is detectable. (Top) 3D-contour plot representation, showing three short cycles: engine's start — accelerations — engine's stop. (Bottom) 3D- landscape plot of the medium cycle. During acceleration peaks, peaking BTX concentrations are also observed.

related species, such as the xylene isomers and ethylbenzene, can be considered as being very similar.

**(C) Discussion.** The results presented clearly demonstrate that the invented electron-pumped rare gas excimer VUV-light-source time-of-flight mass spectrometer is, in principle, a versatile analytical technique for on-line analysis of complex mixtures. Even with the here-presented nonoptimized prototype, a detection limit in the low-parts-per-million (v/v) range was achieved for some aromatic species (Table 3, Figure 6B). Because the ionization is very soft, fragile compounds, such as aliphatic compounds, are ionized without fragmentation (Table 2, Figure 6A). Furthermore, different SPI selectivities can be adjusted by changing the gas-filling of the lamp and thereby the wavelength (Table 1, Figure

3). The instrument prototype already is rather compact (Figure 4), and finally, it was shown that the technique can be applied for fast, quantitative on-line measurement of organic compounds, for example, in exhaust gases (Figures 7 and 8).

Thus, already in its present form SPI-TOFMS with an electron-pumped rare gas excimer VUV lamp as light source might be an interesting alternative or supplement to other on-line mass spectrometric approaches, such as the laser based REMPI-TOMS method or CI-MS techniques.

Furthermore, a substantial potential for optimization was identified in this work. In particular, the optical system for collection and in-coupling of the VUV light can be considerably improved. The 4 W VUV light flux of the lamp during a light pulse

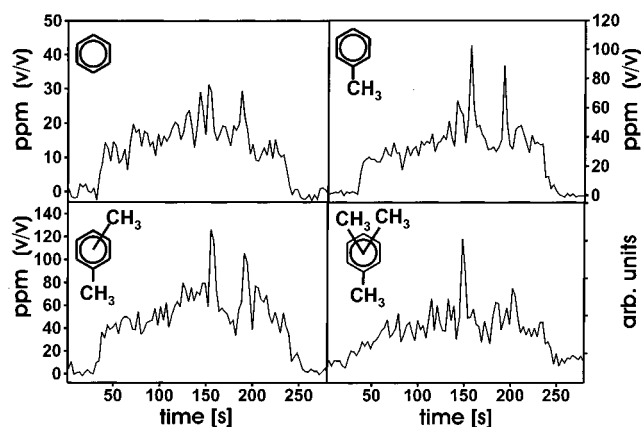


Figure 8. Calibrated concentration–time profiles of benzene, toluene, xylenes, and trimethylbenzenes from the motorcycle exhaust gas measurement by electron-beam-pumped excimer-lamp SPI-TOFMS ( $\text{Ar}_2^*$ ,  $\lambda_{\text{cent.}} = 126 \text{ nm}$ ). The calibration of benzene and toluene was performed directly via the calibration standard (external calibration).

corresponds to  $2.6 \times 10^{18}$  photons/s ( $\text{Ar}_2^*$  excimer). With a XUV detector with an active field of  $20 \text{ mm}^2$  (IRD Inc. type AXUV-20) placed in the ionization region of the TOFMS, a photon flux of  $2.3 \times 10^{14}$  photons/s was detected during the VUV light pulse. This corresponds to a light collection factor of only  $8.8 \times 10^{-5}$ . Thus, the optical system, including the focusing lens, gained only a 10-fold increase of the light intensity in the ionization zone with respect to the intensity obtained by the  $4\pi$  radiation of the light-emitting spot. The reason for the weak collection efficiency was an unsuitable coating of the parabolic mirror as well as a nonoptimal position of the light-emitting spot in the parabolic mirror. Theoretically, a light-collecting efficiency of 0.01–0.2 should be achievable if the mismatching geometrical setup and the mirror coating properties are adapted carefully. This means that a 100-times increase in the detection sensitivity should be achievable with an optimized optical layout.

Improving the optical in-coupling of the VUV light is also necessary for the optimization of the mass resolution, because one cause for the rather weak mass resolution is the poorly focused VUV light in the ion source. The spatially broad irradiation of VUV photons into the ion source leads to poorly defined spatial starting conditions of the formed analyte ions for time-of-flight analysis.

A substantial part of the time-of-flight broadening, however, is due the temporal profile of the VUV radiation pulses. After switching off the lamp because of inactivation of the electron beam, the VUV emission intensity decays with a half-life time in the range of several microseconds, depending on the type of the rare gas and its density.

The decay time is determined by the gas kinetics and the radiative lifetime of the excimer states. Excited atoms form excimer molecules rather rapidly by three body collisions with neighboring atoms. Initially formed rare gas ions contribute to the excimer formation via the formation of ionic excimers and subsequent recombination. Because of a rather low rare gas density in our systems, recombination is rather slow and is responsible for the microsecond decay time of the light pulse in the described excimer light sources. In general, all gas kinetic steps proceed more rapidly at higher gas densities, and the light

pulse in the high-pressure limit is determined by the lifetimes of the triplet state of the excimer molecules.<sup>26</sup> A more detailed description of excimer formation and decay following pulsed particle beam excitation, for example, in the case of xenon, has been reported.<sup>36</sup>

As a result of the slow decay of the VUV light intensity, there is still substantial ion formation in the ion acceleration phase, causing mass peaks with tails toward higher masses (i.e., to higher flight times). This phenomenon is clearly visible in Figures 5, 6, and 7. To minimize the mass peak broadening due to the time profile of the excimer radiation, several strategies can be applied. First, the decay half-life can be minimized by adapting the pressure of the rare gas. Second, ion optical measures can be undertaken. For example, the extraction pulse width can be shortened, and the acceleration voltage can be increased. This, however, requires an already optimized optical setup (i.e., to have a well-defined time-of-flight starting point). Note that an optimization of the mass resolution will also further increase the detection sensitivity of the method.

The primary repetition rate (i.e., the primary acquisition rate of mass spectra) in the here-shown experiments was 120 Hz. The transients of 60 primary mass spectra were accumulated and written to the mass storage device with a repetition rate of 2 Hz. The limiting factor for the repetition rate is the maximal data acquisition rate of PC transient recorder card. The TOFMS repetition rate, however, can be considerably increased if the VUV light source is operated in a continuous mode (cw, not pulsed) or is pulsed with kilohertz repetition rates and a data acquisition scheme based on single ion counting is applied. With this approach, primary TOFMS repetition rates of 20 kHz are feasible.

In addition, more sophisticated alternative coupling concepts can be realized. One of these advanced coupling techniques is the concept of orthogonal acceleration time-of-flight mass spectrometry oa-TOFMS.<sup>37–40</sup> With an oa-TOFMS approach, the VUV lamp can also be operated in a continuous mode. A primary ion source forms a cw-ion beam, which is then pulsed by a secondary ion source into the TOF mass analyzer.

Other alternatives are techniques that allow a temporal accumulation of the ions prior to the mass analysis step. These concepts include time-of-flight mass spectrometers with a storage ion source in which the ions are enriched in a static potential hollow prior to extraction into the TOFMS<sup>41,42</sup> as well as hybrid instruments combining a ion trap storage source where ions are collected in a high-frequency field (Paul trap)<sup>43</sup> with a reflectron

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time-of-flight mass spectrometer.<sup>44–46</sup> In the latter approach, the ion cloud is injected after an enrichment time from the Paul trap into the TOFMS for mass analysis.

However, these methods are rather sophisticated and possibly preferably suited for laboratory-based systems. For process gas monitors based on the electron-beam-pumped-excimer VUV lamp TOFMS, probably direct couplings (such as the one described in this work) will be most suited after careful optimization. For applications that do not require high time resolution or that require only the monitoring of one or a few mass traces, quadrupole mass spectrometers may also be applicable.

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Summarizing, the presented concept, namely the use of electron-pumped excimer lamps for single photon ionization time-of-flight mass spectrometry will allow the realization of simple, compact, and robust gas analyzers for fast on-line (trace) detection of organic compounds. Potential application fields range from industrial applications (process control, quality control) to environmental monitoring (e.g., environmental protection authorities) via civil protection (detection of chemical warfare agents or explosives) to medical application (e.g., breath analysis) and applications in applied and fundamental research.

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