Time of Flight Mass Spectrometry (TOFMS) Using Single Photon Ionisation (SPI) via Particle Beam Induced VUV Excimer Light

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Particle beam excitation of rare gases is an efficient way for VUV light production via the formation and decay of excimer molecules [1,2,3]. Detailed studies of excimer emission from ion beam excited rare gases have been performed [4]. Based on these studies a novel light source has been invented in which low energy electron beams are used for producing VUV light emission [1]. Here we describe one of the first practical applications of such a light source: Photoionization in a time of flight mass spectrometer (TOFMS).

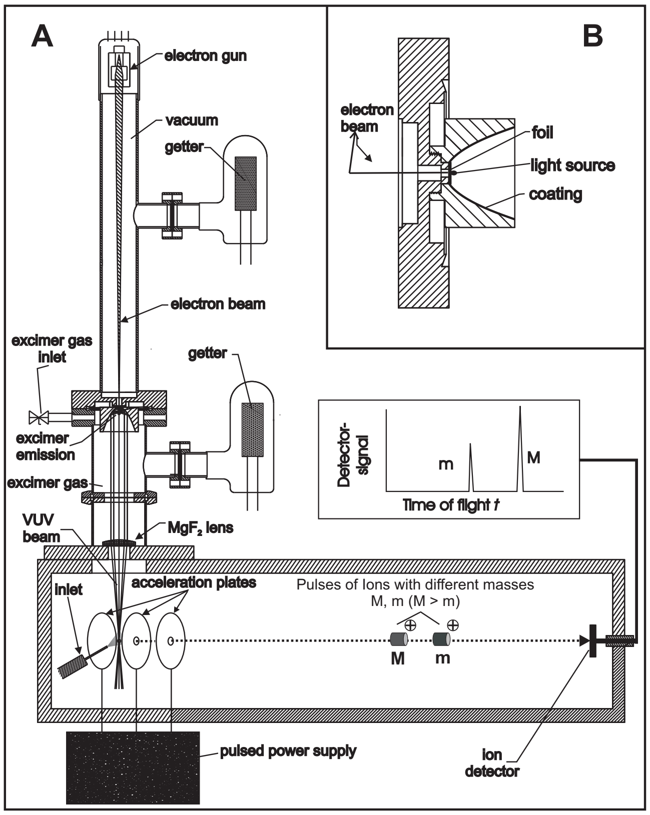

Fig. 1: Schematic drawing of the experimental setup. Part A shows the electron beam induced VUV light source shining down into the time of flight mass spectrometer through a MgF_2 lens which focuses the light to the sample gas inlet between a set of extraction plates. Ions produced by SPI are accelerated and fly along the drift space between the plates and the detector shown to the right. A mass spectrum with the lighter ions (m) arriving earlier than the heavier ones (M) is also schematically indicated. Part B shows and enlarged view of the part of the setup where the VUV light is produced. Here the e-beam comes from the left and is sent into dense rare gas through a thin SiN_x window. The small (mm size) light emitting region is surrounded by an Al-MgF_2 coated parabolic mirror for collecting the light.

The short wavelength of rare gas excimer light sources emitting in the 100 to 200nm region, corresponding to photon energies between 6.2 and 12.4eV, allows photo ionization via the absorption of a single photon (SPI) for a large variety of analyte gases. Compared with other ionization methods such as electron beam or thermal ionization, SPI is a "soft" ionization method which can be applied for non- destructive detecting of complex molecules. Compared with other detection techniques for complex molecules such as gas chromatography SPI TOFMS is a fast detection technique which can be used for online monitoring e.g. in environmental studies or industrial manufacturing processes. An example of such an application is shown below.

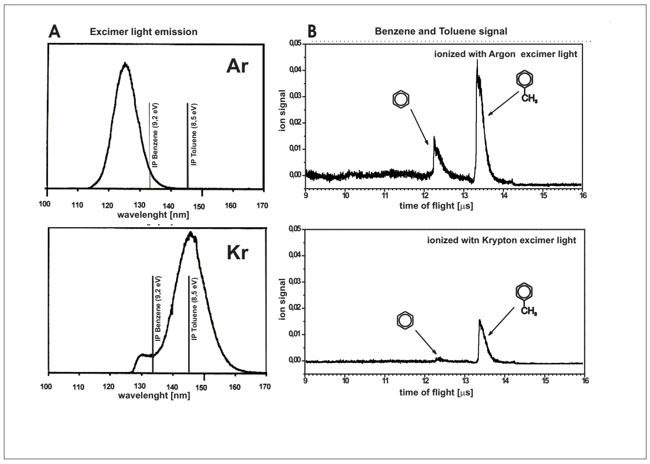

Fig. 2: Time of flight mass spectra of the same analyte gas samples containing benzene and toluene B. Data were recorded using different gas fillings in the VUV lamp, Ar and Kr, respectively. The VUV emssion spectra are shown to the left A. The wavelengths corresponding to single photon ioization of benzene (ionization potential 9.2eV, left mark on the wavelength scale) and toluene (ionization potential 8.5eV, right mark on the wavelength scale) are indicated. This leads to the selectivity for the two species in the TOFMS spectra found in B. The peak on the left side in TOFMS spectra corresponds to benzene, the one on the right side to toluene.

The VUV light source developed at the Tandem laboratory was combined with a time of flight mass spectrometer from the Forschungszentrum für Umweltforschung und Gesundheit (GSF), Neuherberg near Munich for first demonstrational experiments. It was successfully used as a potential alternative for a complex laser system in which short wavelength light (118nm) is produced via frequency tripling of the third harmonic (355nm) of a Nd:Yag laser (1064nm) [5,6].

The combined setup is shown in Fig. 1 (A). The light source was operated with a pulsed 12keV electron beam sent through a 300nm "thick", 1mm^2 silicon nitride entrance window into dense argon and krypton gas leading to brilliant light emission on the so called second excimer continua with center wavelengths of 126 and 150nm, respectively. Gas pressures of typically 1bar were used leading to emission spectra shown in Fig. 2 (left hand side) which are completely dominated by these second continua. The conversion efficiency from electron beam power into light is about 40% for these excimer light sources. The

VUV light was collected and focused into the vacuum of the mass spectrometer via a parabolic VUV mirror and a MgF_2 lens.

A compact linear in-line time of flight mass spectrometer (TOFMS) with a field free drift region of 634mm was used for the analytical measurements. Sample inlet was via differential pupming on a 0.32mm diameter, 1m long fused silica capillary. Gas inlet directly from atmospheric air into the vacuum of the mass spectrometer is possible with this arrangement. An advantage of SPI with photon energies below 13eV is that air can be used as a carrier gas since oxygen and nitrogen is not ionized. Ions of the traces of analyte gas were formed by shining the VUV light onto the gas stream near the exit of the capillary. The ions were extraced by 350ns long, 3kV pulses applied to the extraction plates in the TOFMS and detected with a dual channel plate detector (MCP).

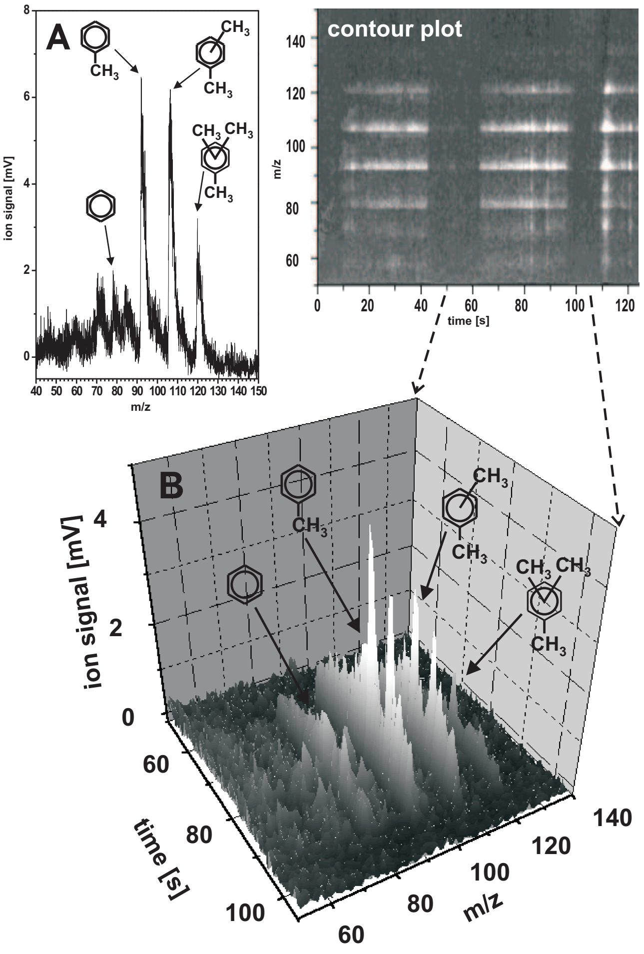

Fig. 3: Mass spectrum of online sampled exhaust gas from a motor bike measured shortly after the engine start using argon excimer light (126nm center wavelength) for photoionization (A). A three dimensional representation of mass spectra versus time for the motor cycle exhaust gas is shown for a 120s periode of time. Some of chemical compounds which could be detected are indicated in the plot B. Data are shown as a contour plot for the full 120s periode and in a perspective view (B) for the expanded time region indicated.

Light emission of the VUV lamp was also pulsed by pulsing the electron beam. Pulses of 8 microseconds were used. The electron beam power was on the order of 10W during these pulses leading to about 4W total VUV light output. Light pulses were synchronized with the extraction pulses of the mass spectrometer and mass spectra were obtained by time dependent recording of the MCP signal of the ion detector. Note, that due to the kinetics of the formation of excimer molecules in the VUV lamp a minimum pulse length on the order of one microsecond has to be used. It was found that making the light pulses somewhat longer and applying the electrical pulse for extracting the ions at the end of the light pulse increases the ion signal in the mass spectra due to accumulation of ions in the extraction region. Details of the experiments described here are discussed in a forthcoming publication [7].

Examples of mass spectra for a sample containing traces of benzene and toluene are shown on the right hand side of Fig. 2. The left side of the figure shows the corresponding emission spectra of the VUV lamp used for the SPI process. The ionization potentials of benzene and toluene are indicated on the wavelength scale. Note that the shorter wavelength emission of argon is capable of ionizing both benzene and toluene whereas the second continuum emission of krypton around 150nm can only ionize the toluene molecules in the sample. This explaines qualitatively the different mass spectra of the same gas sample. The sensitivity for benzene and similar anlyte gases was tested to be on the 10ppm level when using an argon lamp, 120Hz repetition rate of the VUV light and extraction pulses and averaging over 500 pulses.

Time dependent online monitoring of the exhaust gas from a motorcycle was performed to demonstrate an application for online measurements. The data are summarized in Fig. 3. A series of complete mass spectra with time resolution on the time scale of a second was recorded. Data were taken with 120Hz pulse repetition rate and each mass spectrum was formed by averaging over 60 pulses. The 126nm argon excimer lamp was used in this experiment. Although the mass resolution of the system is not yet optimized, benzene, toluene, xylenes, ethylbenzene, and trimethylbenzene can readily be identified in the spectra which were recorded shortly after starting the engine of the (Yamaha 43F) motor cycle. Several acceleration cycles were induced during the 120s time during which data were recorded. This can clearly be seen in the contour plot shown in the upper right corner of Fig. 3. Data in Fig. 3 show the highly dynamical behaviour of the exhaust gas emission demonstrating the necessety for a fast analytical measuring technique for such environmental studies.

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