Fast Pulsed Laser Induced Electron Generation for Electron Impact Mass Spectrometry

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Z. Naturforsch. **43a,** 1151–1153 (1988);
received November 23, 1988

A new ultra fast electron impact (EI) ion source is presented that produces a very short, high intensity electron beam, allowing medium resolution mass spectra to be recorded without pulsing the ion accelerating voltages in a time-of-flight mass spectrometer (TOF-MS). The ion source requires minimum modification of any TOF-MS equipped with an electrostatic ion reflector and UV-laser. EI-spectra are presented for comparison with literature spectra.

The time-of-flight mass spectrometer with laser induced multiphoton ionization (MUPI-TOF-MS) used in our laboratory has already been described [1]. The unique features of this instrument include high mass range, ionization in a collisionless environment (no adduct ions, no influence of matrix on fragmentation patterns), selective and very efficient ionization by resonant MUPI, the possibility to change the fragmentation from soft to hard by merely adjusting the ionizing photon density and simultaneous collection of all ions.

A desirable feature for the instrument would be a simple electron impact (EI)-source with sufficient sensitivity to monitor neutral molecules introduced into the supersonic jet [2]. Electron impact ionization complements the selective resonant MUPI, in the sense that all compounds are ionized, ionization efficiencies do not vary greatly from one compound to the next, large libraries of EI spectra are readily available and unknown spectra can be interpreted by well established rules.

These features are of utmost importance to the qualitative and quantitative analysis of unknown mixtures with coupled chromatography-MS techniques. The belief that our instrument could provide the extraordinary sensitivity required for the new generation of high resolution chromatographic techniques (capillary LC [3, 4], capillary zone electrophoresis [5] and micellar electrokinetic capillary chromatography [6]) gave the final impetus for the design of this novel combined MUPI/EI-source.

The ion source is shown schematically in Figure 1. The modification required for EI-ionization consists merely of a 0.25 mm Ta wire held in place between the repeller and the first extraction lens of the ion source at an electric potential intermediate to that of the two mentioned plates. The wire crosses both the molecular beam and the laser beam normally used for MUPI and is perpendicular to both these beams.

When photons with an energy higher than the work function of Ta (4.25 eV) hit the wire, a swarm of electrons instantaneously leave the surface according to the photo-electric effect. These electrons are accelerated to the repeller and ionize incoming sample molecules in the supersonic jet. Molecules closer to the wire at the time of the electron pulse are ionized with less energetic electrons than those nearer the repeller. However, the point of incidence not only defines the electron energy, but also the initial electric potential of the ion formed in the accelerating field. By adjusting the voltage on the ion reflector to selectively reflect ions of limited kinetic energy (and therefore initial electric potential) [7], narrow peaks can be obtained at the detector. This procedure automatically puts an upper limit to the energy available for EI-ionization events that lead to ions actually transmitted to the detector.

The spectra shown in Figs. 2a–c are representative of our very first results obtained with this source. The 250 nm wavelength photons were obtained from the unfocussed, frequency doubled output of an excimer pumped dye-laser. The energy per pulse was measured at 50 μJ and the energy flux was estimated at 5×10^5 W/cm^2. By realigning the laser beam (without focussing) to just miss the Ta wire, all ions in the spectra disappeared completely, thereby eliminating the possibility of a contributing photoionization process. The reflector was set to transmit ions created by electrons with less than 50 eV energy only.

Conversion of the source to MUPI conditions merely requires the reintroduction of the laser beam focussing lens for the higher flux conditions with si-

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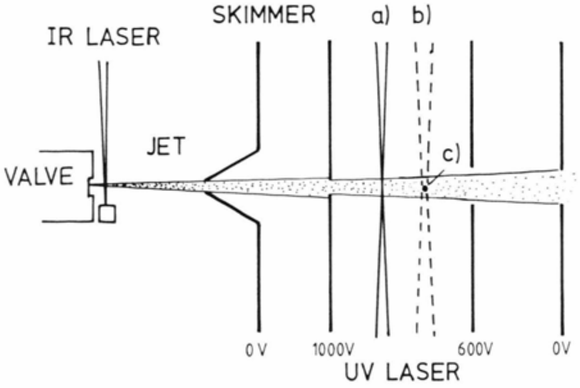

Fig. 1. Scheme of the combined multiphoton ionization – electron impact ionization source. a) UV-laser beam for multiphoton ionization; b) UV-laser beam for electron ionization; c) Ta wire for electron generation.

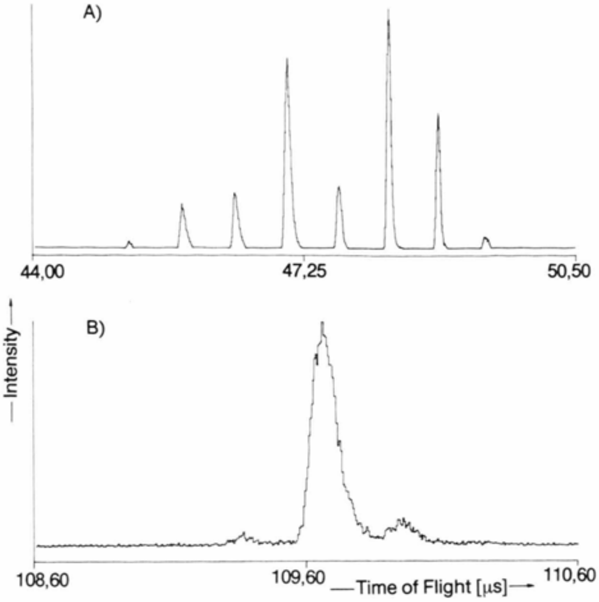

Fig. 3. Raw data of the molecular region from propene (A) and caffeine (B).

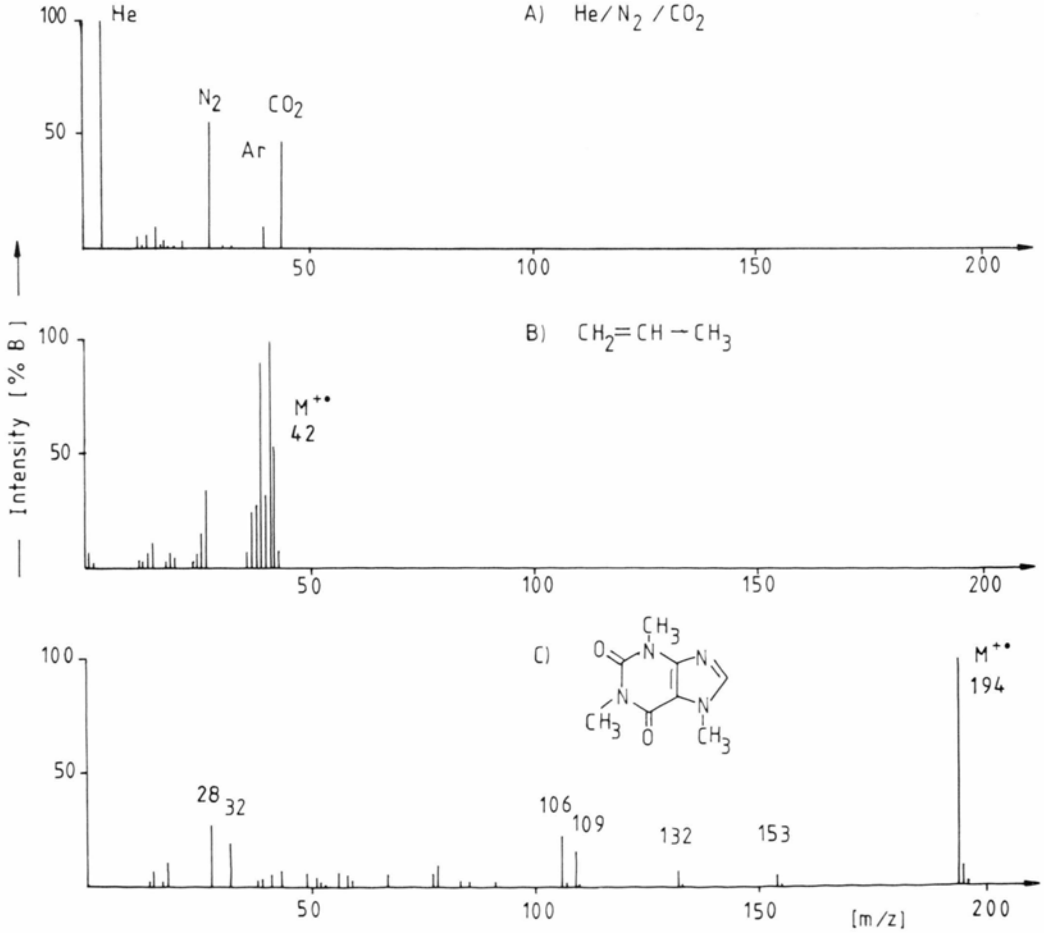

Fig. 2. Mass spectra obtained from laser induced electron impact ionization. A) mixture of Helium, Nitrogen, Argon and CO_2; B) propene (Helium signal suppressed); C) caffeine (Helium signal suppressed).

multaneous shifting of the ionizing beam to just miss the Ta wire.

Figure 2a shows the mass spectrum of a mixture of He, N_2, Ar and CO_2 introduced via the pulsed valve. It represents the accumulation of ions from 100 laser shots and clearly demonstrates that ionization occurs by electron impact.

Figure 2b shows the accumulation of 100 spectra of propene in He gas, introduced via the pulsed valve. The spectrum is nearly identical to literature EI spectra.

Figure 2c shows the accumulation of 100 EI spectra of caffeine, introduced into the pulsed molecular beam of He via IR-laser desorption from the probe tip indicated in Figure 1 [8]. The spectrum shows good correlation with literature spectra and displays a molecular ion with enhanced intensity. This very desirable feature – also observed with other compounds – is probably due to the low temperature of the molecules in the supersonic beam rather than the slightly lower electron energies involved in the ionization process. This phenomenon has been observed before in mass spectra obtained from various organic compounds in cooled beams [9].

Figure 3a–b shows the raw data of the molecular ion region from the propene and caffeine spectrum displayed in Figures 2b–c. This gives a good indication of the resolution – although reduced compared to that obtained with MUPI-spectra – achievable with the EI source.

We are aware of previous attempts to produce short, high current density pulses of electrons by laser beam interaction with metals [10, 11]. In these cases, electron beams in the microsecond timescale could only be obtained because the thermionic electron emission dominates when photon energies are involved that lie below the work function of the metal. By contrast, we observe a very narrow He^+-peak (20 ns FWHM). Also there is a drastic reduction in ion yield when photons with longer wavelength than the threshold 292 nm are used. This proves that we are utilizing the pure photoelectric effect. When the visible fundamental output of the dye-laser was cointroduced into the ion source, very wide peaks and Ta-ions appeared in the mass spectra, indicative of the thermal origin of the electrons under these high power, low photon energy conditions. It is interesting to note that an improved performance of a continuous beam EI-source was recently achieved by laser enhanced thermionic electron emission [12]. In this case a visible, CW-laser beam was directed on the heated tungsten-filament of the ion source.

Acknowledgement

E. R. Rohwer wishes to thank the Alexander von Humboldt foundation for financial support during 1988. R. C. Beavis was supported by a NATO post-doctoral fellowship. This project is supported by grants from the Bundesministerium für Forschung und Technologie (13N5307-2) and the Deutsche Forschungsgemeinschaft (GR 917/1–2).

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