

Picosecond and Nanosecond Laser Ionization for the On-Line Analysis of Combustion-Formed Pollutant

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1. Introduction

A novel apparatus based on Time of Flight Mass Spectrometry (TOF-MS) was recently developed and successfully applied for the on-line analysis of light gases and polycyclic aromatic hydrocarbons (PAH) from atmospheric pressure combustion systems [1].

The interest in the analyses of these species is linked to their high environmental impact. In particular, PAH have cancerogenic and mutagenic effects and moreover they have often been invoked as important intermediates in the chemical processes leading to soot formation [2, 3]. In this work, in order to increase the detection mass range of combustion-formed species and to reduce the parent peak fragmentation caused by hard ionization through electron impact (EI), laser sources have been employed for ionization.

Laser ionization, under appropriate experimental conditions, can be a very efficient process, and when combined with the high ion transmission of a time of flight mass spectrometer, excellent sensitivity can be achieved [4].

A Nd:Yag Nanosecond laser at two different wavelengths, corresponding to the forth and the third harmonic (266 and 355 nm, respectively), have been used allowing to detect PAH and water clusters up to 2000 u. The water clusters furnished a calibration of the system in a molecular weight range much larger with respect to that obtained with standard molecules generally used for this purpose.

However, if an electronically excited molecule relaxes to a lower-lying state before it absorbs a second, ionizing photon, a loss of ionization efficiency may be observed. Some relaxation phenomena, such as internal conversion and intersystem crossing can occur on very rapid, subnanosecond, time scales [5, 6]. In theory, this problem can be overcome increasing the intensity of laser pulse, but it can cause fragmentation.

On the other hand, if the laser pulse is short compared to the time scale of these relaxation events, photoionization should be favored compared to them and the ionization efficiency of a molecule with a very short excited-state lifetime should improve.

Therefore, in this work, laser ionization with subnanosecond pulses (in the picosecond range) was also exploited in order to test if further reduction of fragmentation and increase of ionization efficiency can be obtained.

2. Experimental

2.1 Set-up

An innovative set-up specifically designed for the on-line detection of combustion products of high masses has been used for the analysis of PAH in an atmospheric-pressure ethylene flame. The experimental set-up is deeper described in a previous work [1].

Basically, it is composed of: (i) a combustion system, (ii) a sampling probe and transfer line, (iii) a supersonic molecular beam, and (iv) a reflectron TOF-MS instrument, designed and built by Kaesdorf s.r.l., where different types of ionization sources can be used.

The TOF-MS system can be operated with a mass filter, a disposal where a pulsed electric field is used to deflect the lowest mass ions. In these conditions, saturation of the MCP due to the very high signal intensities produced by the most abundant low-mass ions is avoided and the dynamic range of the detector is preserved.

For EI, the electrons are produced by a hot tungsten loop filament. In the present experiment a pulse duration of 2 ms with a repetition rate of 20 Hz was used for EI, in order to use the same frequency of the laser, for a strict comparison between the two ionization methods.

Photoionization was performed using the 3rd (355 nm) and the 4th (266 nm) harmonics of a Nd:YAG pulsed laser (Brilliant model Y18B; Quantel SA, Les Ulis, France) with a repetition rate of 20Hz and pulse duration of 7 ns. The maximum peak energies were 70 mJ for the 3rd harmonic and 10 m J for the 4th harmonic. The fluences were $1.7 \cdot 10^{13} \text{W/cm}^2$ and $3.2 \cdot 10^{12} \text{W/cm}^2$ for the 3rd and the 4th harmonics, respectively.

Short pulses photoionization was also employed by using the 3rd (355 nm) harmonic of a Nd:YAG pulsed laser (Leopard Series model D-20; Continuum, Santa Clara, CA - USA) with a repetition rate of 20Hz and pulse duration < 20 ps. The maximum peak energies were 10 mJ for the 3rd harmonic. The fluence is $4 \cdot 10^{14} \text{W/cm}^2$.

2.2 Samples

As combustion pollutant source, a fuel-rich ethylene/oxygen laminar premixed flame was used, produced by a McKenna burner. A water-cooled stainless-steel probe (2mm i.d.), connected to a suction pump, was used for the sampling of combustion gases. The sampled mixture was guided by a 3mm (i.d.) steel tube from the probe up to the vacuum chambers of the TOF-MS system. The sampled gases enter the first chamber of the instrument through a solenoid actuated valve (General Valve Corp.) equipped with a 0.8mm aperture nozzle generating a pulsed supersonic jet. The valve has been modified in order to minimize the dead volume and to increase the suction efficiency. The central part of the jet is extracted by a skimmer to produce a pulsed molecular beam.

As water clusters source, a reservoir with distillate water was used. It was kept at a temperature of 28 °C in nitrogen atmosphere. Since the temperature-induced fluctuations of the water temperature can affect the cluster formation, it is continuously measured with a copper-constantan thermocouple and is kept constant within 1 °C during all the experiment.

3. Results and discussion

In this work the ethylene/oxygen premixed laminar flame was operated at a ratio C/O=0.65, just below the soot formation threshold (C/O=0.66), to reduce the risk of probe orifice occlusions by high soot loads. The spectra of flame products have been acquired sampling at a height of 6mm above the burner, where the concentration of PAH is at a maximum.

In a previous work [1], the mass spectra were obtained in the same conditions but employing EI at an electron energy of 70 eV. In those spectra strong signals were detected at $m/z < 100$, with a maximum around benzene (m/z 78), followed by the typical ion distribution of PAH from naphthalene (m/z 128) up to ovalene (m/z 398).

In the present work, laser ionization with nanoseconds pulses at two UV wavelengths (266 and 355 nm) and with picoseconds pulses (355 nm) have been employed instead of EI, in order to perform a softer ionization of combustion products.

The use of the mass filter strongly reduces the signals below m/z 50. For this reason in the following the mass spectra have been reported starting from this m/z value.

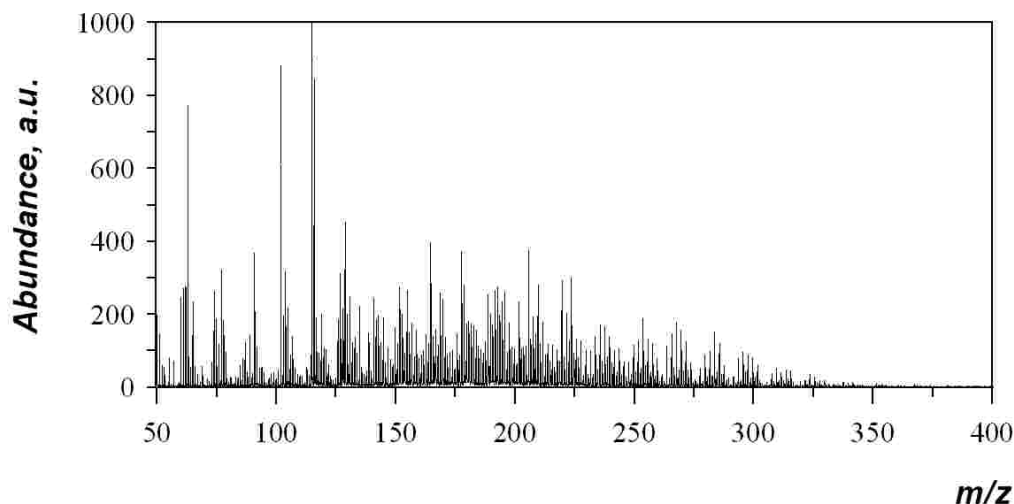


Fig. 1 TOF-MS spectrum of combustion products acquired at $z=6\text{mm}$ height above the burner with nanosecond laser light at 266 nm.

In Fig. 1 the mass spectrum with nanosecond laser at 266nm is reported. It shows a different distribution of ion signal intensities from that obtained with EI [1], according to the results reported in [7]. In fact, the most abundant ions in this case are around naphthalene (m/z 128) and the ions in the mass range m/z 50–100 are not as abundant as they are in the EI spectrum. As in the EI case, the production rate falls for m/z values >400 .

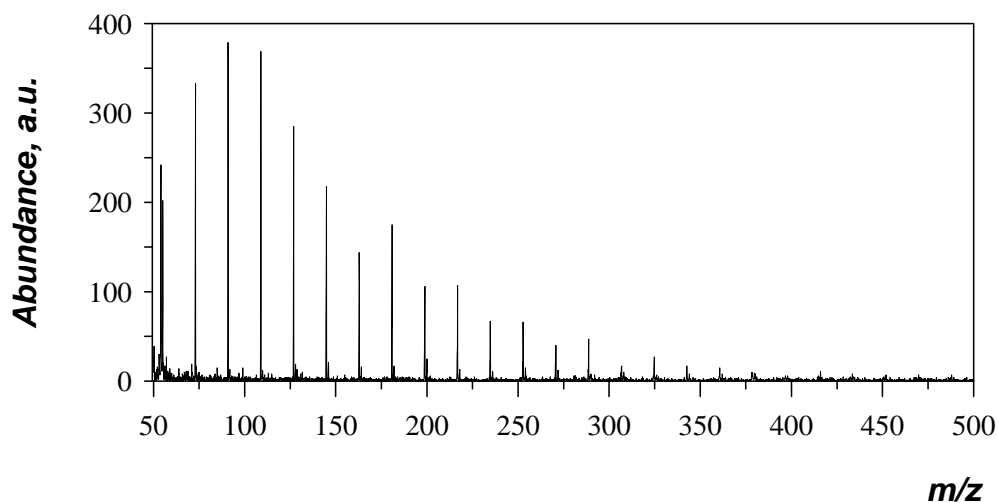


Fig. 2 TOF-MS spectrum of combustion products acquired at $z=6\text{mm}$ height above the burner with nanosecond laser light at 355 nm.

Figure 2 shows the TOF mass spectrum acquired with nanosecond laser ionization at a wavelength of 355nm. In this spectrum, the sequence of the PAH is submerged by the sequence of ions with a gap of 18 m/z units. The sequence has been interpreted in previous work [1, 8] as due to water clusters probably formed after the expansion in the nozzle, in the first chamber of TOF apparatus from water molecules formed in combustion reaction.

This sequence is highly reproducible and extends up masses of about 2000 u, which is much above the masses presented by noble gas mixtures typically used for calibrating on-line TOF apparatus (136 u). Therefore, producing in a controlled and reproducible way the water cluster series can be very useful in order to calibrate the TOF-MS system in a very larger MW range than usual.

The water clusters have been reproduced using as source, instead of combustion water,

distillate water from a reservoir where a nitrogen flow, bubbling inside the liquid, acts as transfer gas. In this way, it is possible to use the clusters for studying and optimize laser ionization performances in a cleaner environment with respect to the flame.

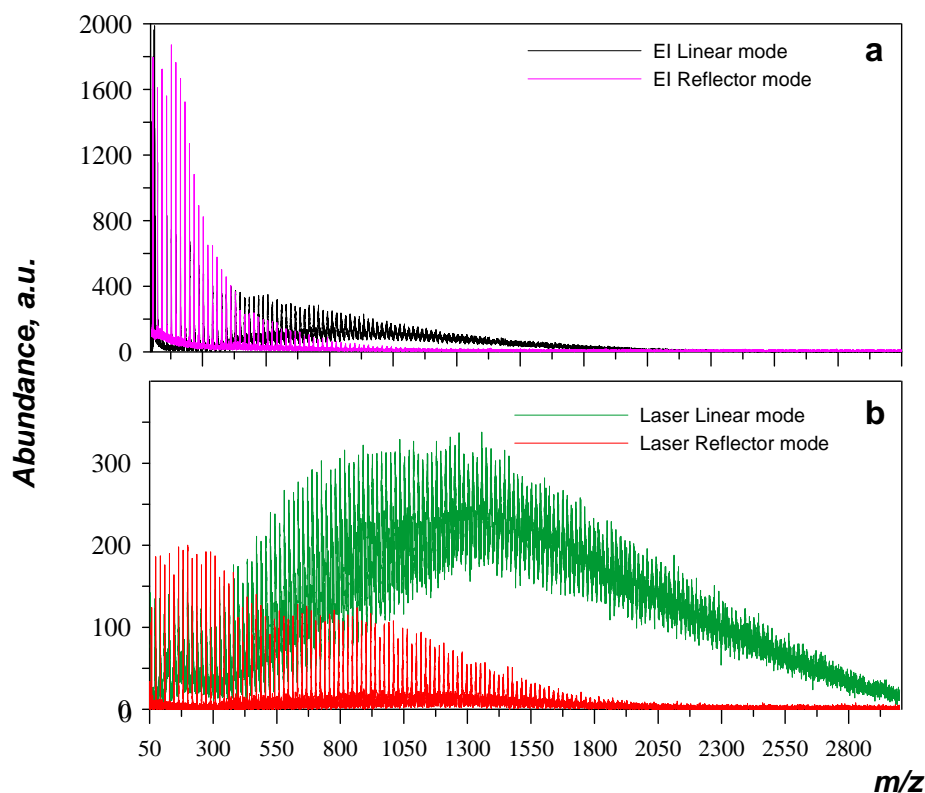


Fig. 3 TOF-MS spectrum of water clusters acquired with EI (a) and with picosecond laser light at 355 nm (b).

Fig. 3 a shows the TOF mass spectra of water clusters acquired by EI both in reflectron and in linear mode whereas in Fig.3b the same spectra are reported as measured by picosecond laser ionization at 355nm.

Fragmentation in the drift region of TOF produces ions with the same velocity as their precursors, and if no additional electrical fields are encountered (as in the linear configuration), they will arrive at the detector with the same flight times as their precursor ions. Thus, if the goal is to determine the MW of large molecules, the linear TOF provides the highest sensitivity [4].

Reflectron acts as an energy-focusing device, compensating kinetic energy distribution of ions, after they have entered in the flight tube, therefore improving mass resolution. In addition to improved mass resolution, reflectron instruments provide the opportunity to obtain structural information from the metastable fragmentation that occurs in the flight tube [4].

Therefore, the possibility of having simultaneously spectra acquired in linear and reflectron mode allows collecting much more structural information on the analytes.

In the specific case of water clusters (Fig.3), it is possible to observe linear spectra extending in a very larger MW range with respect to reflector ones, by using both the ionization methods. This is compatible with a fragmentation occurring into the flight tube with the result of both reducing the high mass signals and increasing the low mass fragment signals in reflector spectra. The great resolution difference between linear and reflectron mode is well observable in Fig.4, where a zoom of the spectra of fig.3a is reported in the range m/z 350-420.

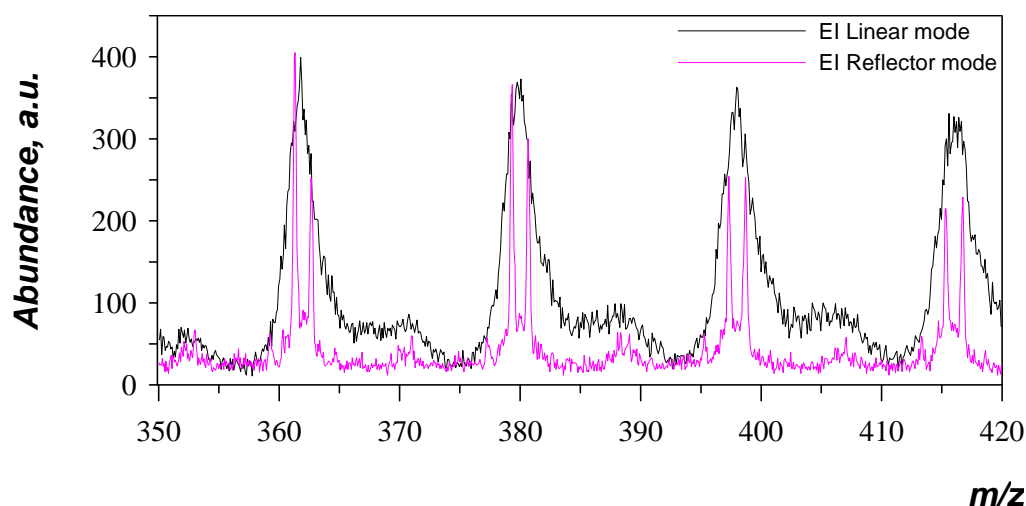


Fig. 4 Zoom of TOF-MS spectrum of water clusters acquired with EI.

A quantitative study of peak position and gaps in the high resolution reflectron spectra is in progress in order to have more information on the clusters from a structural point of view.

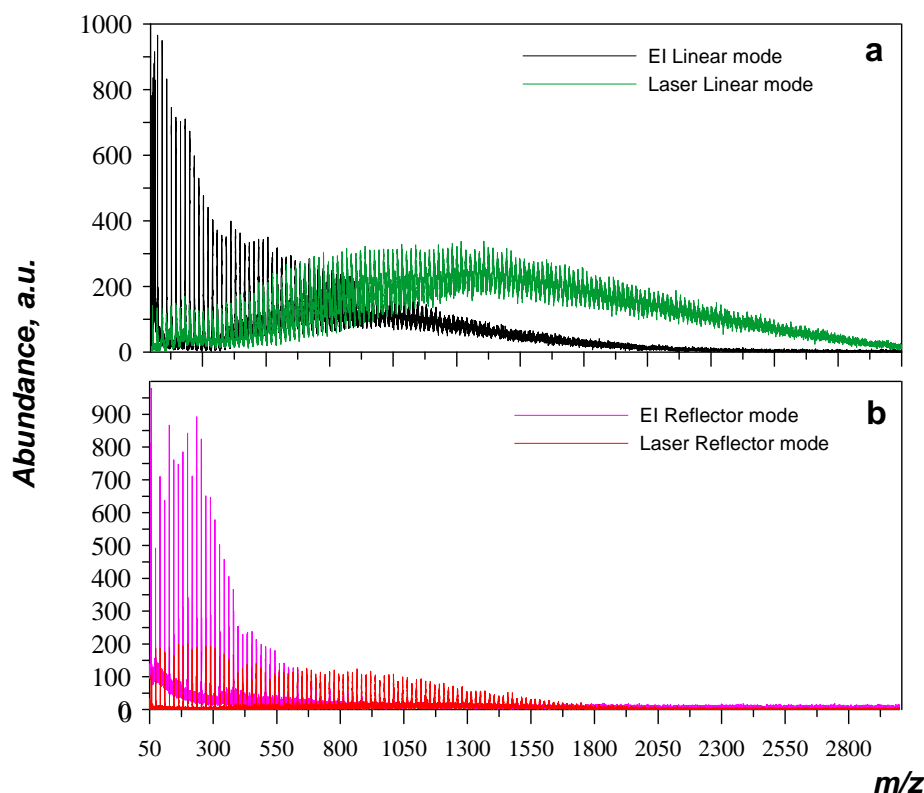


Fig. 5 TOF-MS spectrum of water clusters acquired in linear mode (a) and reflector mode (b) with EI and with picosecond laser light at 355 nm.

The comparison between EI and picosecond laser ionization is reported in Fig.5 in the same TOF configuration (linear in Fig.5a and reflectron in Fig.5b). It is evident in the Fig. 5 that the MW range observable by picosecond laser ionization is much larger with respect to EI, with both the configuration, extending up to 3000 u whereas EI spectrum arrives up to about 2000 u in linear configuration. This difference is interpretable with a large clusters fragmentation occurring in the ionization region when a hard ionization system like EI is employed.

It is noteworthy to observe that by using nanosecond laser as ionization source (Fig.2) no

difference were observed in the MW range detected with respect to EI ionization, suggesting that the shorter pulses of the picosecond laser can limit the fragmentation occurrence.

The result is very encouraging and allows us to speculate that also for combustion pollutant ionization the use of picosecond laser instead of the nanosecond one could help to extend the detection range from the PAH up to nanoparticles and this will be matter for a future work.

4. Conclusions

In order to increase the detection mass range of combustion-formed species and to reduce the parent peak fragmentation caused by hard ionization through EI, laser sources have been employed for ionization in an advanced TOF-MS apparatus.

A Nd:Yag Nanosecond laser at two different wavelengths, corresponding to the forth and the third harmonic (266 and 355 nm, respectively), have been used allowing to detect PAH and water clusters up to 2000 u. The water clusters furnished a calibration of the system in a MW range much larger with respect to that obtained with standard molecules generally used for this purpose.

A Nd:Yag Picosecond laser at 355 nm allows to extend the water clusters detection range up to 3000 u, showing a large decrease of fragmentation occurrence with respect to both EI and nanosecond laser ionization.

A quantitative analysis of peak position and gaps, also by using a Fourier Transform approach, recently developed for spectra interpretation [1] is now under study as well as the application of picosecond ionization source to combustion pollutant spectra.

5. Acknowledgments

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6. References

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