Analysis of PAH Mass Spectra Periodicity by Fast Fourier Transform

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In this work we present a new methodology for the analysis of complex combustion products mass spectra in terms of fundamental periodicities detected by Fast Fourier Transform (FFT) Mass The spectra have been acquired by a Time of Flight Mass Spectrometer (TOF-MS) on–line to a premixed laminar ethylene/Oxygen flame looperating at atmospheric pressure. The extracted gases were diluted with inert gas and carried to the ion source in molecular beam conditions. Electron impact ionization (EI) and photoionization with laser radiation from a Nd:YAG nanosecond pulsed laser at two different wavelengths in the UV range (266 nm and 355 nm) have been achieved. The corresponding mass spectra and the the relative mass periodicities have been compared. The mass spectra obtained using laser wavelength of 355 nm and EI present a mass series of peaks regularly spaced 18 Th that can be used for the system calibration and to test the FFT analysis method.

1. Introduction

More than 50% of the total mass of the ultrafine atmospheric aerosols are carbonaceous material present as primary and secondary aerosols . Beside natural sources, combustion systems strongly contribute to the formation of this material in the atmosphere. Moreover, the formation mechanisms of all the products emitted from combustion systems are not yet well known so in the actual research many efforts are dedicated to understand the formation and the growth processes of these products, in particular of the higher molecular weight species like Polycyclic Aromatic Hydrocarbon (PAH) and soot (Bockhorn, 1983).

Mass spectrometry plays an important role in chemistry, physics, and metrology. It is used to identify unambiguously complex mixtures and molecular species in, e.g., petrochemical, analytical, or bioanalytical and combustion studies. In many cases the complex spectra are very difficult to understand, especially when mixtures of compounds are analyzed.

In this work we propose a new methodology to analyze the PAH mass spectra in order to reach a dipper understand of the growth mechanisms of large molecules in combustion systems. The main idea is to analyze the PAH sequences by applying FFT to mass spectra collected on line to a premixed laminar flame and to individuate periodicities that can indicate preferential growth root and/or fragmentation patterns. The mass spectra have been obtained by a TOFMS apparatus directly on line with an atmospheric pressure flame employing different kinds of ionization sources: electron beam and laser light in the UV (Panariello et al., 2008).

The paper is organized as follows: Section 2 is dedicated to a brief description of the principle of the FFT and to a discussion on the possible interpretation of the data. In Section 3 we describe the TOFMS experimental apparatus. Section 4 is dedicated to the analysis of the mass spectra and the FFT spectra of combustion products collected from a C/O=0.6 ethylene/oxygen flame. Concluding remarks and future perspectives are reported in Section 5.

2. Fast Fourier Transform

The Discrete Fourier Transform (DFT) is a mathematical operation transforming one discrete function of the independent variable into another function, which is the representation of the original function in the domain of the inverse of the independent variable.

In our case the independent variable is represented by the mass and therefore the Fourier transform will be function of (1/m). The DFT requires an input function that is discrete and whose non-zero values have a limited (finite) duration, moreover the data should be equally-spaced. The TOFMS data are not equally distributed due to the fact that the time of flight is proportional to the root square of M (Cotter, 1943). Therefore the input function should be created by interpolating the experimental data uniformly with a resolution comparable with the minimum instrumental resolution.

The DFT only evaluates enough frequency components to reconstruct the finite segment that was analyzed. Therefore it is often said that the DFT is a transform for Fourier analysis of finite-domain, discrete-time functions. The sinusoidal basis functions of the decomposition have the same properties.

The DFT can be computed efficiently in practice using a Fast Fourier Transform FFT algorithm.

Since FFT algorithms are commonly employed to compute the DFT, the two terms are often used interchangeably. However "DFT" refers to a mathematical transformation, regardless of how it is computed, while "FFT" refers to any one of several efficient algorithms for the DFT evaluation.

The FFT is a discrete Fourier transform algorithm which reduces the number of computations needed for N points from $2N^2$ to 2NlgN, where lg is the base-2 logarithm, respect to the discrete Fourier Transform.

If the input function has a N data points and the time separation between successive abscissas is Δt, then the nth frequency (f_n) datum is:

$$f_n = \frac{n}{N\Delta t}$$

and the frequency domain will also have N points with the maximum observable frequency, f_{max}

$$f_{Max} = \frac{n}{\Delta t}\left(1 - \frac{1}{N}\right).$$

3. Experimental

In Figure 1 the complete experimental setup is reported. It is composed by a combustion system, a sampling probe and a transfer line, a supersonic molecular beam a reflectron TOF-MS, where different types of ionization sources can be used. An ethylene-oxygen laminar premixed flame stabilized on a water-cooled sintered bronze burner (McKenna burner, d = 60 mm) was used as combustion system. A water-cooled stainless-steel probe, shown in Figure 1, connected to a suction pump was used for sampling of the combustion gases. The pumping rate can be optimized to realize isokinetic conditions. A more detailed description of the experimental set up is reported in a previous work (Panariello et al., 2008).

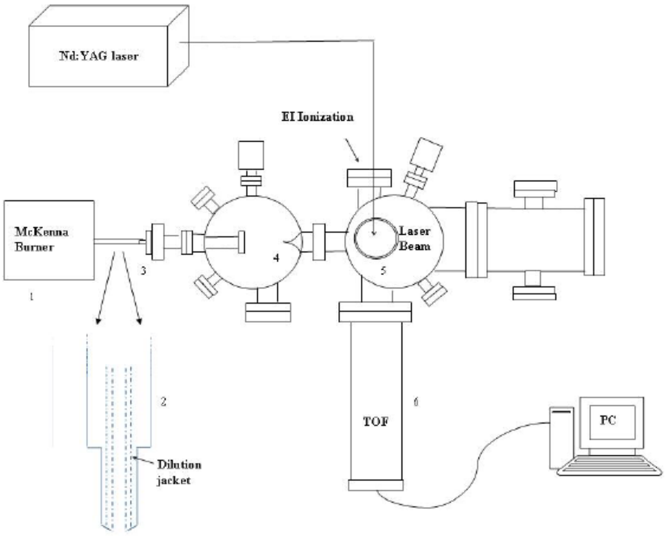

Figure 1: TOFMS apparatus scheme: a combustion system (1), a sampling probe (2) and a transfer line (3), a supersonic molecular beam system (4), an ionizing chamber (5) and a Reflectron Time of Flight Mass Spectrometer (6).

Measurements presented in this paper where acquired by using a mass filter reducing the signal corresponding to m/z lower that 50 Th.

For the E.I. the electrons are created by a hot tungsten loop filament. The electron energy used in this work was 70 eV and the repetition rate 100 Hz. Photo-ionization has been performed using the 3th (355 nm) and the 4th (266 nm) harmonic of a Nd:YAG pulsed laser (Quantel, Brilliant; model Y18B) with a repetition rate of 20 Hz and pulse duration of 7 ns. The maximum peak energy was 70 mJ for the 3th harmonic and 10 mJ for the 4th harmonic. Both harmonics beams have been focused into the ionization chamber by means of a convex lens of 21 cm focal length.

4. Results

In order to check for the presence of repeated chemical structures we have applied the FFT analysis to the mass spectra data. The detection of periodicity in mass spectra is very important as it allows to formulate hypotheses about the growth mechanism of combustion products. The application of FFT to mass spectra makes possible a simple and accurate analysis also when the spectra appear very complex as in the case of combustion product spectra.

In Figure 2 a) we have reported mass spectra of water clusters from 54 Da up to 400 Da obtained with laser ionization at 355 nm. The FFT method has been preliminarily validated on the water clusters mass spectrum, that present a highly periodic mass spectrum: the FFT method has been applied on the equally spaced spectrum and the intensity of the transformed function has been evaluated as function of the inverse of the frequency (1/m) and reported as function of the corresponding mass periodicity, m in Figure 2b) where it is possible to observe that a very big peak corresponding to the periodicity of 18 Da, as expected. The relative higher harmonics (2^{nd}, 3^{rd},…) are also present in the spectra.

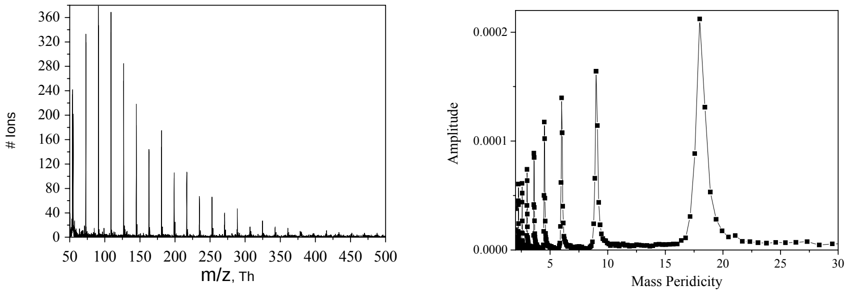

Figure 2: a) Water Cluster Mass spectra and b) Fourier transform periodicity spectra.

The FFT has been applied to the whole spectra obtained by ionizing both with EI and by laser at 266 nm the product of a slightly sooting flame with a C/O ratio of 0.6 at 6 mm above the burner.

We have reported in Figure 3 a) the whole mass spectrum obtained with the EI . In Figure 3 b) the FFT of the mass spectrum is reported and several periodicities can be observed: around 5.5, and 9 Da, a remarkable peak at 14 Da with a shoulder at 13 Da and a wider structure extending from 20 up to 40 Da.

The components of periodicity between 5.5 Da, 6.5 Da and 9 Da are probably due to double ionization of the sequences spaced by 11, 13 and 18 Da, which correspond to the addition of a C atom and CH_2 to de-protonated PAH and of a water molecule, respectively.

The high signal around 14 Da can be representative of radical addition reactions (addition of CH_2).

The structure extending from 20 up to 40 Da includes different periodicities, as 24 Da and 26 Da that do not appear as single peaks due to the large contribution of protonated PAH parent ions ([M+H]+ , [M+2H]+) or C^{13} isotope of PAH.

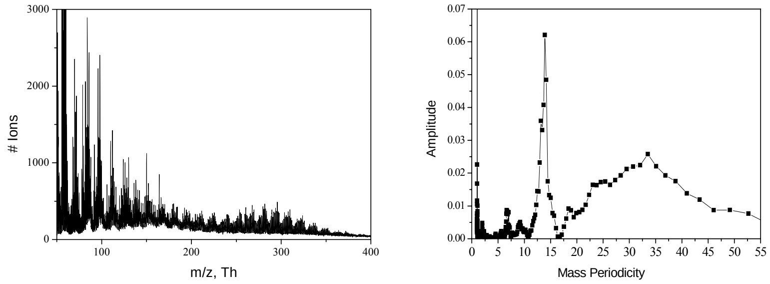

Figura 3:a) C/O=0.6 flame mass spectrum obtained with Electron Impact; b) Corressponing FFT mass peridicity spectra over the all mass range detected.

All the features observed in Fig. 3 (b) can be interpreted hypothesizing the presence of two sequences. The first sequence is due to PAH with an even number of carbon atoms (even-C-numbered PAH) with a difference in molecular mass corresponding to net sequential addition of C_2 as an ethylene bridge (24 Da gap), i.e. addition of C_2H_2 followed by hydrogen elimination. Another sequence is also present corresponding to C or/and CH_2 addition (12 and 14 Da gap, respectively). It can be ascribed to odd-C-numbered PAH containing cyclopenta-fused rings coming from the insertion of a methylene (-CH2-, 14 Da gap) into a bay region of angular PAH (Keller et al, 2000). The gap at 26 Da can be due to the isomerization of the formed PAH through hydrogenation (globally an addition of C_2H_2) similarly to what found by Beck et al. (Beck et al., 1999).

These results are in agreement with off-line mass spectrometric analysis of samples collected in premixed flames (Apicella et al, 2007; Ciajolo et al, 1982; Happold et al, 2007) and in jet-stirred-plug-flow reactor (Lafleur et al, 1996).

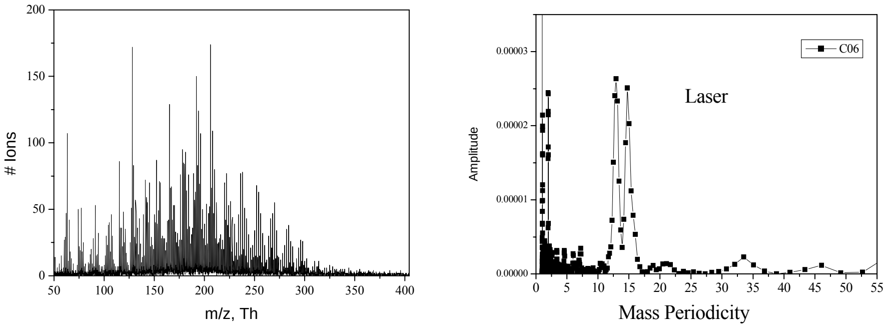

Figura 4: a) C/O=0.6 flame mass spectrum obtained with λ=266 nm; b) Corressponing FFT mass peridicity spectra over the all mass range detected.

The complete mass spectrum obtained with the laser ionization at λ=266 nm is reported in Figure 4 (a); in Figure 4 (b) we have also reported the corresponding FFT mass periodicity.

Figure 4 (b) shows a remarkable contribution of sequences spaced by 11 Da, 13 Da. These periodicities can be interpreted as due to the addition of a C atom between the sequences of PAHs with odd and even number of carbon atoms. In the case of odd-C-numbered PAH the presence of a methylene bridge causes the most intense ions are constituted by de-protonated [M-H]+, [M-2H]+or protonated [M+H]$^+$, [M+2H]$^+$ parent ions, as reported in literature (Keller et al, 2000 ; Happold et al. 2007), whereas for even-C-numbered PAHs the predominant ion is [M]+. This corresponds to 11 Da and 13 Da gaps between consecutive peaks group.

A similar mechanism can be hypothesized for the addition of CH_2 to the PAHs with an odd and even number of carbon atoms bringing to the periodicity of 13 and 15 Da.

Moreover, the presence of isotopic PAHs (PAHs with at least one C^{13}) contributes to the 13 Da gap. A small peak at 24 Da can suggest the insertion of C_2 between consecutive peaks of the same sequences, as explained before, but with this ionization method we can observe that this contribution is much less predominat. This is indicative of the different ionization process and need to be better understood.

All the above presented results on periodicities are in agreement with the most reliable models on PAHs growth mechanisms reported in literature. Indeed, the addition of C_2 corresponds to reaction with acetylene occurring through the gain of two carbon atoms, as described in the HACA mechanism (Frenklach, 2000). The presence of a sequence of odd-C-numbered PAH due to the addition of a C atom is in agreement with the soot inception model proposed by Zhang et al. (1983). his mechanism assumes that large polycyclic aromatic molecules tend to maximize carbon-carbon bonding by incorporating pentagons into their aromatic bonding network. These pentagons generate a curvature which brings the net back on itself to form a spheroidal shell which, in turn, can close to form a spherical soot particle.

5. Conclusions

On line TOFMS analysis of combustion products on-line to an atmospheric-pressure premixed laminar flame in slightly sooting conditions, has been presented. EI and UV photo-ionization (at wavelengths of 355 nm and 266 nm) have been employed to obtain mass spectra of high mass molecular structures formed in flame.

Mass spectra of water clusters produced in the expansion process have been obtained with EI and photoionization at 355 nm and used to calibrate (Panariello et al, 2008) and to test the FFT method.

The FFT analysis has been applied to all the mass spectra obtained to detect the periodic sequences of mass spectra of combustion gas, which are very important for making hypothesis on PAHs growth mechanism.

All the features observed can be interpreted hypothesizing the presence of two peak sequences. The first sequence is due to PAHs with an even number of carbon atoms with a difference in molecular mass corresponding to net sequential addition of C_2 as an ethylene bridge (24 Da gap), i.e. the addition of C_2H_2 followed by hydrogen elimination. Another sequence of peaks is also present corresponding to C or/and CH_2 addition (12 and 14 Da gap, respectively). It can be ascribed to odd-C-numbered PAH containing cyclopenta-fused rings coming from the insertion of a methylene The other gap at 26 Da can be due to the isomerization of the formed PAH through hydrogenation (globally an addition of C_2H_2). These results are in agreement with off-line mass spectrometric analysis and the most reliable models on PAHs growth mechanisms reported in literature. However, the use of FTT as shown in this paper, allows to detect not only even periodicity as reported in literature, but also odd periodicity that gives more insights to PAHs structure interpretation.

6. Acknowledgments

This work has been carried out in the framework of the research agreement between CNISM Consortium and Consiglio Nazionale delle Ricerche. The authors want also to thank the Centro di Competenza Analisi e Monitoraggio del Rischio ambientale for the finantial support for the TOFMS system.

7. References

Apicella B, Carpentieri A, Alfè M, Barbella R, Tregrossi A, Pucci P, Ciajolo A. 2007, Proceedings of the Combustion Institute; 31, 547.

Beck MT, Keki S, Szabo PT, Zsuga M. 1999, Tetrahedron; 55: 1799

Bockhorn, H., 1994, Soot Formation in Combustion: Mechanisms and Models, Springer-Verlag, Berlin

Ciajolo, A., R. Barbella, M. Mattiello and A. D'Alessio, 1982, Proceedings of The Combustion Institute. 19, 1369.

Cotter, R.J., 1943, Time-of-flight Mass Spectrometry: Instrumentation and applications in biological research. ACS, Washington, DC.

Frenklach M., 2002, Phys. Chem. Chem. Phys. 4, 2028-2037.

Happold, J., H.H. Grotheer and M. Aigner, 2007, Rapid. Commun. Mass Spectrom. 21, 1247.

Lafleur AL, Taghizadeh K, Howard JB, Anacleto JF, Quilliam MA., 1996 J. Am. Soc. Mass Spectrom., 7,276

Ledman, D.W., and R.O. Fox, 1997, J. Am. Soc. Mass Spectrom. 8, 1158.

Keller, A., R. Kovacs and K.H. Homann, 2000, Phys. Chem. Chem. Phys. 2, 1667-1675.

Kovacz, R., S. Loffler and K.H. Homann, H. Bockhorn, Ed., 1994, Soot Formation in Combustion. Springer, Berlin Heidelberg, New York.

Panariello, M., B. Apicella, A. Bruno, M. Armenante and N. Spinelli, 2008, Rapid Commun. Mass Spectrom. 22, 573.

Zhang QL, O'Brien SC, Heath JR, Liu Y, Curl RF, Kroto HW, Smalley RE. Stuke M. 1986, J. Phys. Chem.; 90 (4), 525.