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آنالیز کمی ترکیبات هیدروکربن در طیف سنجی تحریک فیلامنتی

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چکیده – مزیت اصلی طیف سنجی فلورسانسی با تحریک فیلامنت لیزری در آشکارسازی چندین نمونه به طور همزمان می باشد. امکانپذیر بودن این گزاره با گزارش روشی برای پایش همزمان آلوده کننده های گازی موجود در جو بر اساس گسیل فلورسانسی ارائه می شود. این نمونه های گازی به وسیله فیلامنتهای ناشی از پالسهای پرشدت لیزر فمتوثانیه ای تحریک می شوند. این تکنیک با آشکارسازی و تشخیص همزمان گازهای جوی همسان متان و استیلن معرفی می شود. طیف یک ترکیب "نامعلوم" که با الگوریتم ژنتیکی تحلیل می شود توافق خوبی با نتایج تجربی با درصد خطای کمتر از ۲۵٪ نشان می دهد.

کلید واژه- طیف سنجی، هیدروکربن، فیلامنت لیزری، الگوریتم ژنتیک.

Quantitative analysis of hydrocarbon mixtures in filament-induced spectroscopy

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Abstract- The main advantage of filament-induced fluorescence spectroscopy is the simultaneous detection of multiple species. The possibility of this interpretation is reported on an approach for simultaneous monitoring of multi-gases pollutants based on fluorescence emission of trace gases, induced by the filamentation of intense femtosecond laser pulses in air. This method is illustrated by the simultaneous detection and identification of similar atmospheric trace gases, methane and acetylene. The spectra of an "unknown" mixture are analyzed with a genetic algorithm, showing good concentrations agreements with the experimental results within an error of 25%.

Keywords: Spectroscopy, Hydrocarbon, Laser Filaments, Genetic Algorithm.

1 Introduction

Laser-based spectroscopic techniques have been extensively employed for sensing atmospheric trace species [1, 2]. However, with these techniques the laser usually may only be optimized for one pollutant at a time. In this paper, we experimentally demonstrate the feasibility of simultaneous detection and identification of multiple trace species in the atmosphere using Filament-Induced Nonlinear Spectroscopy (FINS). It has been previously illustrated that the peak intensity inside a femtosecond filament is about 5×10^{13} W/cm^2 during the laser pulse propagation in air because of the intensity clamping [3, 4]. With this high intensity, most molecules inside the filament can be dissociated and undergo fragmentation. Small fragment products are excited and emit characteristic fluorescence, which could be used as spectral fingerprint for identifying the parent molecules [5].

In this work, using FINS, the fluorescence spectra of air at atmospheric pressure containing the trace gases, methane (CH_4) and/or acetylene (C_2H_2), with different concentrations were recorded. An arbitrary mixture of these two gases in one atmospheric air were then prepared as an 'unknown' case and the fluorescence spectra of this 'unknown' were taken. Using a genetic algorithm, the species and concentration of the "unknown" could be identified using the stored database to within a precision of 25%.

2 Experiment

The experiment was conducted with a Ti:Sapphire femtosecond laser system. The laser pulse, characterized by a repetition rate of 10 Hz, a duration of 45 fs and the central wavelength at 807 nm, was focused into a 1.5-m long gas cell equipped with fused silica windows (figure 1).

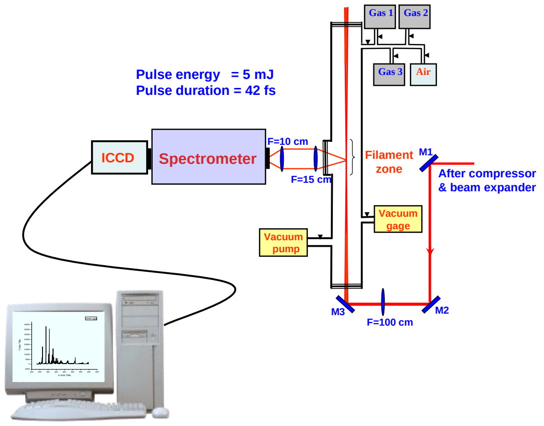

Figure 1: Experimental setup. See the detailed description in the text.

According to our design, we used mixtures of CH4 and air, C_2H_2 and air or (CH_4 + C_2H_2) and air at atmospheric pressures with variable concentrations. The dispersed fluorescence was detected using a gated intensified charge coupled device (ICCD). For fluorescence decay measurements, a photomultiplier tube (PMT) with a rise time of 0.2 ns was connected to the spectrometer.

3 Results and discussion

Figure 2 shows two typical filament-induced fluorescence (FIF) spectra of air at atmospheric pressure containing ~ 5263 ppm of CH_4 (Figure 2a) and ~ 1316 ppm of C_2H_2 (Figure 2b). Analysis of the spectra in Figure 2 shows that, besides the emission coming from N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) and N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$) produced by the nitrogen molecule in air [6], some small molecular fragments, originating from the interaction of the trace species with the femtosecond laser pulses, can be observed farther than 400 nm.

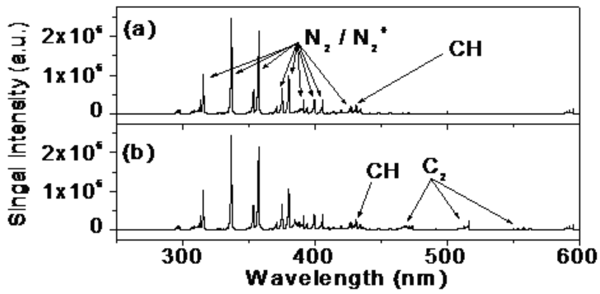

Figure 2: Typical FIF spectra of air containing (a) 5263 ppm of CH_4 or (b) 1316 ppm of C_2H_2.

However, due to the low concentration of the trace species and the strong N_2/N_2^+ spectral background in air, the signals of species are covered by the nitrogen signals in less than 400 nm. Then it is difficult to analyze the characteristic fluorescence using these two spectra. In order to get more insight into the characteristics of these fluorescence spectra, an effective approach to attenuate the background signals is to perform delayed time-resolved measurements to reject the nitrogen fluorescent signals [5]. In this case, the gate delay of the ICCD was set to t = +7 ns and all other experimental parameters were kept as above. By using such a delayed detection, the characteristic fluorescence signals can be clearly observed, as shown in Figure 3a and 3b for CH_4 and C_2H_2, respectively.

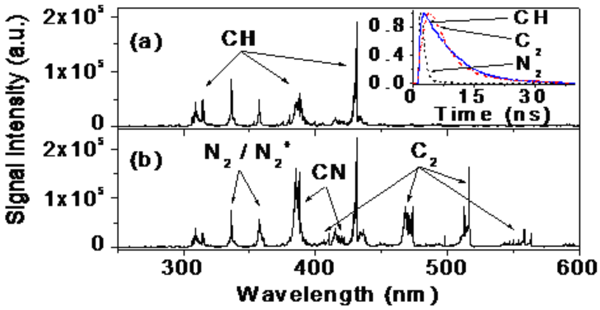

Figure 3: Time-resolved FIF spectra of air containing (a) 5263 ppm of CH_4 or (b) 1316 ppm of C_2H_2 with a delay time of +7 ns. The inset shows the fluorescence decays of N_2, CH and C_2 at 337, 431 and 516 nm, respectively.

In Figure 3a, the three spectral bands around 430, 390 and 314 nm are assigned to the $A^2\Delta \rightarrow X^2\Pi$, $B^2\Sigma^- \rightarrow X^2\Pi$ and $C^2\Sigma^+$- $X^2\Pi$ transitions of the CH radical, respectively [7]. In Figure 3b, the spectral bands in the regions of 563, 516, and 471 nm are assigned to the Swan band of C_2 and the spectral band around 408 nm is assigned to the Deslandres-D'Azambuja band of C_2 [7]. The spectral region around 388 nm contains the spectral signatures of different molecular fragments, which might be the $B^2\Sigma^- \rightarrow X^2\Pi$ transition of CH, Deslandres-D'Azambuja band of C_2 and the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of CN [7]. In Figure 3, we can see that the nitrogen signals are now much weaker. This is because the N_2/N_2^+ signals have a very short lifetime (< 1 ns), whereas the characteristic fluorescence of the trace molecules observed in this work has the lifetimes of about 6-8 ns, as shown in the inset of Figure 3.

Besides time-resolved measurements, another way to minimize the background signals is to subtract a pure air spectrum from the contaminated air spectra (not shown).

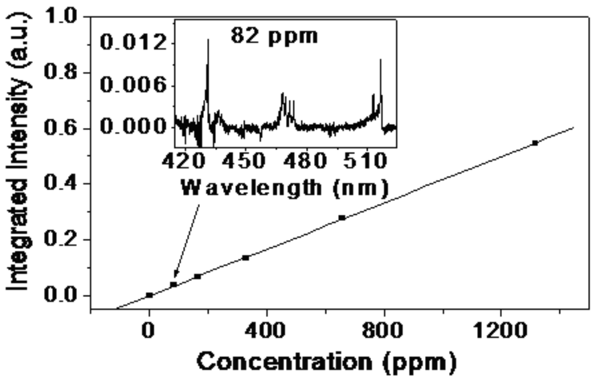

Figure 4: The fluorescence signals integrated over 428.2-431.7 nm, 465.1-474.2 nm and 504.4-517.0 nm (rectangular points) as a function of C_2H_2 concentration. The inset: the FIF spectrum with a C_2H_2 concentration of 82 ppm.

Figure 4 shows the fluorescence signals as a function of the C_2H_2 concentration (solid rectangles) obtained by subtracting the air background spectrum. The inset of Figure 3 shows the spectrum for the C_2H_2 concentration of 82 ppm. The CH and C_2 bands can still be clearly observed. As a result, we obtained the 3σ (σ is the standard deviation of the background noise level) detection limits of 1 ppm and 280 ppb for CH_4 and C_2H_2, respectively. The results of 3σ detection limits for time-resolved ones are 2 ppm and 350 ppb for CH4 and C_2H_2, respectively. Thus, using FINS, the detection limit can be down to the ppm–ppb level.
To check the feasibility of multi-constituents identification, we recorded the spectra of CH_4 (5263 ppm) + C_2H_2 (1316 ppm) mixed in air at atmospheric pressure with the delay time of t = -7 ns (Figure 5a) and t = +7 ns (Figure 5b). A genetic algorithm was used to analyze them under the assumption that the trace species and concentrations in the mixture are unknown. Before this measurement, the spectral signatures and the signal strengths for CH_4 and C_2H_2 at different concentrations at these two delay times have been individually stored into the genetic algorithm database. A description of the genetic algorithm can be found elsewhere [8]. In this work, using a LabView-based genetic algorithm program, all the spectra in the database were normalized to the nitrogen signal at 337 nm. The algorithm created a first generation of random mixtures based on the spectra in the database. A test function was applied to evaluate and sort the random spectra according to their fitness to the "unknown" spectra. Genetic mutations and gene crossovers random techniques were used to evolve the sorted spectra over generations. The process is shown in the Figure 6.

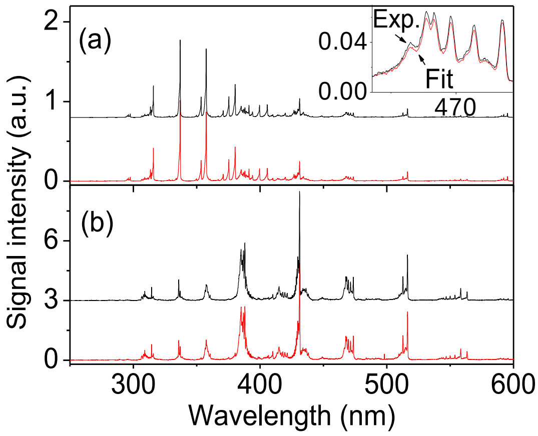

Figure 5: The FIF spectra of air containing 1316 ppm of C_2H_2 and 5263 ppm of CH_4 with the time delays of (a) t = -7 ns (top) and (b) t = +7 ns (top) and their fits (bottom). The inset: the experimental (Exp.) and fitting (Fit) spectra with t = -7 ns.

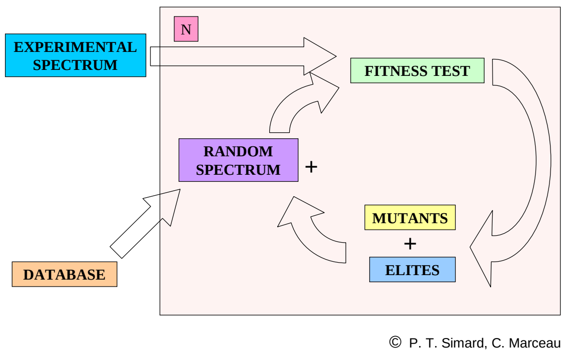

Figure 6: Sketch of genetic algorithm.

As shown in Figure 5, the experimental “unknown” spectra are fitted very well by the genetically calculated spectra after only ~50 generations. The calculated concentrations are $C_{methane}$ = 6342 ppm and $C_{acetylene}$ = 1592 ppm for the delay time of t = -7 ns and $C_{methane}$ = 4697 ppm and $C_{acetylene}$ = 1539 ppm for the delay time of t = +7 ns, respectively, which are in good agreements with the experimental results with the errors of less than 25 % (experimental concentrations: $C_{methane}$ = 5263 ppm and $C_{acetylene}$ = 1316 ppm).

4 Conclusion

Using FINS, we experimentally demonstrate simultaneous detection and identification of two ‘unknown’ trace gases in the atmosphere with detection sensitivity in the ppm-ppb concentration range. The genetic algorithm can be used to identify the unknown spectra with the premise that a spectral database including the spectral signatures and the strengths of the signals of the corresponding trace species is built. The agreement between calculation and experiment observed in the specific case of methane and acetylene opens the door for a future performance of triple or, more generally, multiple species atmospheric sensing.

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