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Simultaneous detection and identification of multigas pollutants using filament-induced nonlinear spectroscopy

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The authors report on an approach for simultaneous monitoring of multigas pollutants based on fluorescence emission of trace gases, induced by the filamentation of intense femtosecond laser pulses in air. The high intensity inside a filament can dissociate the gas molecules into small fragments which emit characteristic fluorescence. This method is illustrated for simultaneously sensing atmospheric trace gases, methane and acetylene. The spectra of an "unknown" mixture were analyzed by using a genetic algorithm, showing good concentration agreement with the experimental results within an error of 25%. *© 2007 American Institute of Physics.*
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Laser-based spectroscopic techniques, such as differential absorption light detection and ranging, tunable diode laser absorption spectroscopy, and laser-induced fluorescence, have been extensively employed for sensing atmospheric trace species because of their high sensitivity, nonintrusiveness, and real-time analysis.[1,2] However, with these techniques the laser usually may only be optimized for one pollutant at a time. In this letter, 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.[3–5] 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.[6,7] In principle, a single laser is sufficient to induce characteristic fluorescence from a large number of molecular species.

Therefore, one may anticipate that simultaneous detection and identification of multiple trace gases in the atmosphere can be achieved by FINS. This is indeed the case as our experiment shows. 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. Concentration measurements demonstrate that the detection limits can reach about 1 parts per million (ppm) and 300 parts per billion (ppb) for CH_4 and C_2H_2, respectively. The spectral signatures and the signal strengths of these two molecules were individually collected and stored in a database. An arbitrary mixture of these two gases in one atmospheric air was 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%. This shows the promising potential of this technique for simultaneous detection and identification of multiple atmospheric constituents. Furthermore, recent advances in the development of ultrafast laser have shown that filamentation can be formed at a distance as far as a few kilometers in the atmosphere.[8] For this reason, we expect that this technique of FINS could be applied to remote multicomponent atmospheric sensing.

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 by a fused silica lens ($f=1$ m) into a 1.5-m-long gas cell equipped with fused silica windows. The laser beam had a radius of $a\approx5$ mm ($1/e$ level of intensity). The distance between the focusing lens and the input window of the gas cell was about 25 cm. According to our design, we used mixtures of CH_4 and air, C_2H_2 and air, or ($CH_4+C_2H_2$) and air at atmospheric pressures with variable concentrations. The fluorescence signal was collected at a right angle to the laser propagation direction; it passes through an 8 cm diameter fused silica window and was imaged by two biconvex quartz lenses ($f=10$ and 5 cm) onto the entrance slit of the imaging spectrometer (Acton Research Corp., Spectrapro-500i). The slit was arranged to be parallel to the laser propagation direction in order to enhance the collection efficiency. The dispersed fluorescence was detected using a gated intensified charge coupled device (ICCD) (Princeton instruments Pi-Max 512). For fluorescence decay measurements, a Hamamatsu R5916U-52 microchannel-plate (MCP) photomultiplier tube (PMT) with a rise time of 0.2 ns was connected to the spectrometer. A Tektronix Model TDS 7254 oscilloscope with a bandwidth of

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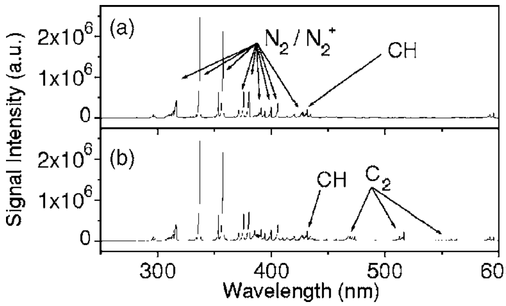

FIG. 1. Typical FIF spectra of air containing (a) 5263 ppm of CH_4 or (b) 1316 ppm of C_2H_2.

2.5 GHz was used to record and average the signals from the MCP PMT.

For spectral measurements, the gate width and the delay time of the ICCD were set to 500 ns and $t=-7$ ns, respectively (note that the laser pulse arrives in the interaction region at $t=0$). The energy per pulse was 6 mJ and the data were averaged over 200 shots. Figure 1 shows two typical filament-induced fluorescence (FIF) spectra of air at atmospheric pressure containing ~5263 ppm of CH_4 [Fig. 1(a)] and ~1316 ppm of C_2H_2 [Fig. 1(b)]. The concentrations have an error of about 5%. It is noteworthy that these two spectra are very clean, that is, free from plasma continuum. This is consistent with previous observations in air.[9] Analysis of the spectra in Fig. 1 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,[9] some small molecular fragments, originating from the interaction of the trace species with the femtosecond laser pulses, can be observed. However, due to the low concentration of the trace species and the strong N_2/N_2^+ spectral background in air, 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.[6] 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 Figs. 2(a) and 2(b) for CH_4 and C_2H_2, respectively. In Fig. 2(a), 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 $C\,^2\Sigma^+ \rightarrow X\,^2\Pi$ transitions of the CH radical, respectively.[10] In Fig. 2(b), 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.[10] 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.[10] In Fig. 2, 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 lifetimes of about 6–8 ns, as shown in the inset of Fig. 2. Therefore, the strong nitrogen contaminations can be "gated" out significantly while the emissions from the fragments remain rather strong.

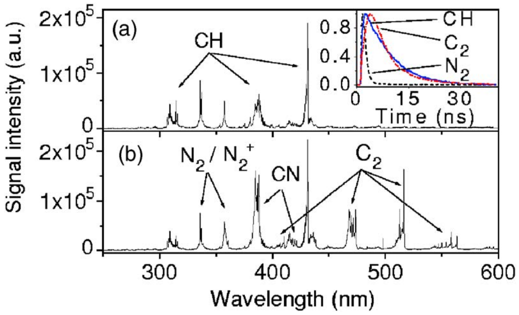

FIG. 2. (Color online) Time-resolved FIF spectra of air containing (a) 5263 ppm of CH_4 or (b) 1316 ppm of C_2H_2 with a delay time of +7 ns. The inset shows the fluorescence decays of N_2, CH, and C_2 at 337, 431, and 516 nm, respectively. The decays at 337 and 516 nm were measured with air at atmospheric pressure containing 1316 ppm of C_2H_2 and the decay at 431 nm was obtained with a mixture of air and CH_4 (5263 ppm).

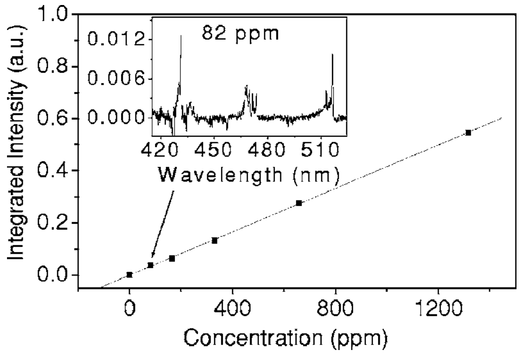

FIG. 3. Fluorescence signals integrated over 428.2–431.7, 465.1–474.2, and 504.4–517.0 nm (rectangular points) as a function of C_2H_2 concentration together with a linear fit (solid line). The inset shows part of the FIF spectrum, by subtracting the air background spectrum, with a C_2H_2 concentration of 82 ppm.

Besides time-resolved measurements, another way to minimize the background signals is to subtract a pure air spectrum from the contaminated air spectra. The characteristic fluorescence signals can be clearly observed as well (not shown). Therefore, the characteristic fluorescence of the fragments obtained without time-resolved measurements can be utilized to analyze the trace constituents. In particular, this method, in contrast to the time-dependent one mentioned above, is still valid for remote sensing of atmospheric species, in which a backward detection scheme is usually employed.

To determine the detection limit under our experimental conditions, concentration measurements were performed. As an example, Fig. 3 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 Fig. 3 shows the spectrum for the C_2H_2 concentration of 82 ppm. The CH and C_2 bands can still be clearly observed. The solid line in Fig. 3 is the calibration curve, which is linear over the concentration range studied. 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 CH_4 and C_2H_2, respectively. Thus, using FINS, the detection limit can be down to the ppm–ppb level, depending on the induced fluorescence efficiency of different trace gas species.

To check the feasibility of multiconstituent identification, we recorded the spectra of CH_4(5263 ppm)

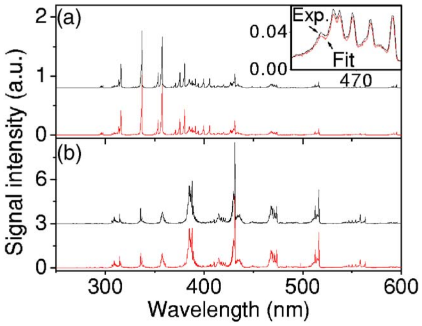

FIG. 4. (Color online) FIF spectra of air containing 1316 ppm of C_2H_2 and 5263 ppm of CH_4 with the time delays of (a) $t=-7$ ns (top) and (b) $t=+7$ ns (top) and their fits (bottom). The inset shows part of the experimental (exp.) and fitting (Fit) spectra with $t=-7$ ns in a higher resolution.

$+C_2H_2$(1316 ppm) mixed in air at atmospheric pressure with delay times of $t=-7$ ns [Fig. 4(a)] and $t=+7$ ns [Fig. 4(b)]. 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.[11] 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 crossover random techniques were used to evolve the sorted spectra over generations. As shown in Fig. 4, the experimental unknown spectra are fitted very well by the genetically calculated spectra after only ~50 generations. The calculated concentrations are $C_{\text{methane}}=6342$ ppm and $C_{\text{acetylene}}=1592$ ppm for the delay time of $t=-7$ ns and $C_{\text{methane}}=4697$ ppm and $C_{\text{acetylene}}=1539$ ppm for the delay time of $t=+7$ ns, respectively, which are in good agreement with the experimental results with the errors of less than 25% (experimental concentrations: $C_{\text{methane}}=5263$ ppm and $C_{\text{acetylene}}=1316$ ppm).

In summary, 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 a door for a future performance of triple or, more generally, multiple species atmospheric sensing.

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