Mid-infrared Broadband Spectroscopy for Plasma Analysis

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Abstract: We demonstrate the application of a home-built Fourier Transform Spectrometer based on a mid-infrared supercontinuum source for multispecies detection in a plasma reactor. The results show the high capability of the system for plasma analysis. © 2022 The Author(s)

1. Introduction

The chemical industry is confronted with the challenge of reducing its carbon dioxide (CO_2) emission. Novel, innovative technologies are needed that enable electrification of chemical processes, which are presently based on use of heating by fossil fuel. One of the best candidates for fulfilling this task is plasma-based gas conversion [1], that is able of efficiently converting two of the common greenhouse gasses, CO_2 and methane (CH_4) into carbon monoxide (CO) and hydrogen (H_2), also known as syngas [2]. However, discharge plasmas consist of numerous (reactive) species, and it is challenging to control the reaction specificity. Therefore, it is of great importance to develop a multispecies detection system capable of analyzing the reactants/products of the plasma for different conditions (e.g. electric discharge power and mixing ratios). Ultra-broadband spectroscopy in the mid-infrared (MIR) wavelength range, where most of the molecular species have their distinct and strong absorption features, has a great potential to be used for this purpose. We have recently demonstrated the potential of the a home-built Fourier Transform Spectrometer based on a novel MIR supercontinuum (SC) source [3] and a multipass absorption cell for multispecies trace gas detection [4]. Here we use this system to monitor the reactants/products of a $CO_2/CH_4/N_2$ discharge plasma.

2. Experimental setup and results

The experimental setup is demonstrated in Fig. 1(a). The plasma reactor is a discharge tube connected to a high voltage power supply. The gas feed is a constant flow (total flow of 2 l/h) of a mixture of $CO_2/CH_4/N_2$ and the mixing ratio between the species can be freely changed. The pressure inside the plasma cell is 25 mbar and the output gas is connected to a multipass cell kept at 16.5 mbar. The SC source is fiber-coupled, with spectral coverage of 3.7-7.7 μm as shown in Fig. 1(b), average power of ~86 mW, pulse duration of ~0.5 ns, and repetition frequency of 3 MHz [3]; and its output is collimated by a parabolic mirror mounted on the multipass cell (effective path length 32 m) via a cage structure. The transmitted beam from the multipass cell is directed towards a custom-build FTS, which is discusses in details in our previous work [4]. Briefly, it is based on a Michelson interferometer; the incoming light beam is split by a beamsplitter into two arms, each leading to a hollow retroreflector mirror. The retroreflector mirrors reflect the beams with slight horizontal and vertical shifts, so that the reflected beams recombine on the beamsplitter and the two resulting superpositions of the beams (interfering pair of beams) can both propagate towards separate photovoltaic detectors. The two interference patterns at the output of the detectors are subtracted from each other by a differential amplifier in a balanced detection scheme, to effectively reduce the relative intensity noise of the SC source. The two retroreflectors are mounted back-to-back on a linear-motor translator stage. Therefore, an optical path difference of 10 cm between the two beams can be reached by scanning the translation stage over a distance of 2.5 cm. This provides a spectral resolution of 0.1 cm^{-1} (3 GHz). A stable He-Ne laser is used to calibrate the optical path difference of the FTS, whose beam is sent alongside the SC beam path in the FTS and the corresponding interferogram is recorded by a photodetector.

In the first experiment, the plasma was generated in a flowing mixture of 50% CO_2 in N_2 by applying a voltage of 17.5 kV with a current of 10 mA (specific energy input 7.1 MJ/mol). In Fig. 1(c), the measured absorbance spectrum of the product gasses is shown (in black); alongside the corresponding fitted simulated spectra (inverted, in color, using parameters from the HITRAN database) include nitrogen dioxide (NO_2, ~154 ppm), nitric oxide (NO,

~0.33%), nitrous oxide (N_2O, ~570 ppm), CO (~14.6%), CO_2 (~13.0%) and H_2O (~1.1%). In the second experiment plasma was generated in a flowing mixture of 30% CO_2 and 70% CH_4 by applying a voltage of 18 kV with a current of 15 mA (specific energy input of 11 MJ/mol). In Fig. 1(d), the measured absorbance spectrum of the product gasses is shown (in black); alongside the corresponding fitted simulated spectra (inverted, in color, using parameters from the HITRAN, PNNL, and GEISA databases) including CO (~32%), CO_2 (~13.9%), ethylene (C_2H_4, ~0.73%), formaldehyde (H_2CO, ~0.13%), acetone (C_3H_6O, ~0.3%), and acetaldehyde (C_2H_4O, ~0.3%). The residuals of the fits are shown in the lower panels in both of the plots.

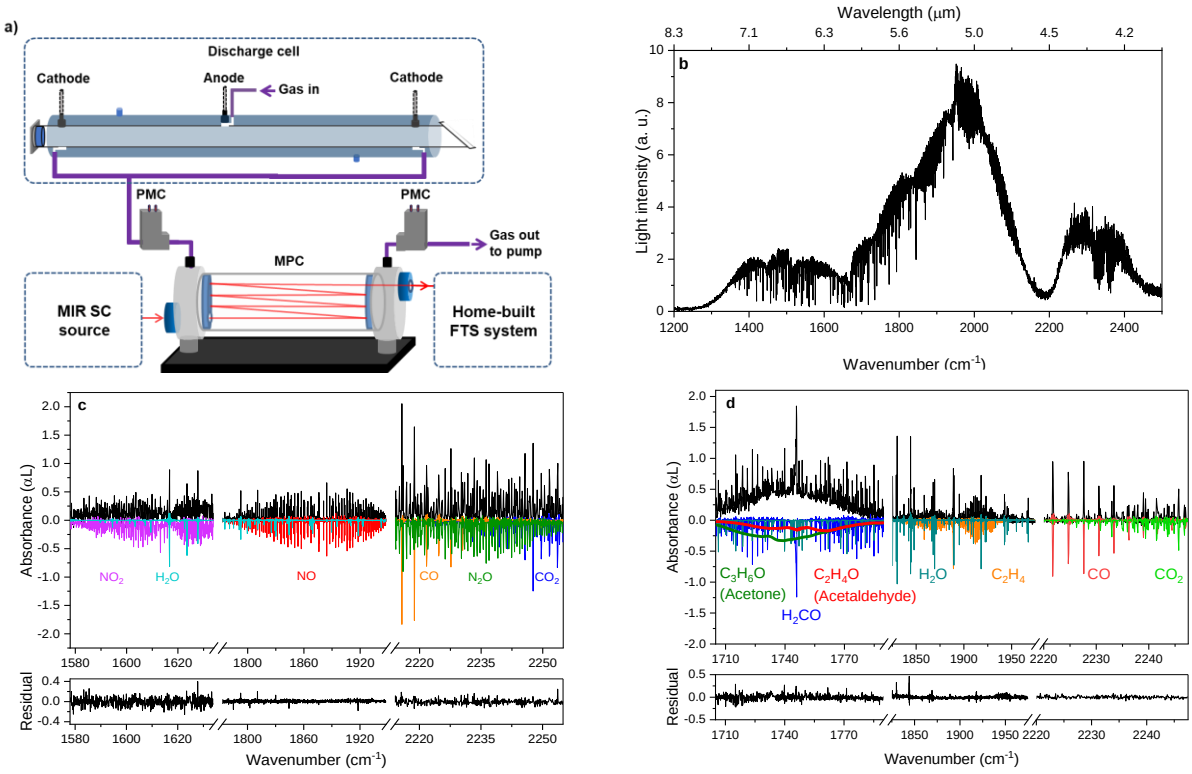

Fig. 1. (a) Experimental setup. MPC: multipass cell, PMC: pressure meter/controller. (b) Spectral coverage of the MIR SC source. (c) Measured spectrum (in black) of products of a plasma of 50% CO_2 and 50% N_2 and the fitted modelled spectra (in colors, inverted). (d) Measured spectrum of the products of a plasma of 70% CH_4 and 30% CO_2 (in black) and the fitted modelled spectra (in colors, inverted).

These measurements demonstrate the ability of the system to detect numerous molecular species created in electrical discharges of $CO_2/CH_4/N_2$, even for the species with overlapping spectral features. By changing the parameters of the plasma, such as specific energy input, and reactant mixing ratio, one can find the best combination of the parameters for maximizing the concentration of a specific produced species. Note that classical FTIRs can also be used for plasma analysis, and they can match the spectral coverage of our system. However, classical FTIRs use thermal sources with relatively low spectral power density, which combined with the high spectral resolution needed for detection of interfering gas species at low pressure, result in very long averaging times. Most importantly, the thermal sources lack spatial coherence, which makes it challenging to create long interaction path lengths (e.g. by using an MPC with a long effective path length) to increase the detection sensitivity. Furthermore, the spatial coherency of SC sources, makes it possible to produce a well-collimated beam with a small beam diameter for in-situ monitoring in long (>1 m) plasma cells, which is also difficult to obtain using thermal sources.

3. References

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