Analysis of Methane and Carbon Dioxide Plasmas with Supercontinuum-based Fourier Transform Spectroscopy

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Abstract: We present the results of a home-built Fourier transform spectrometer based on mid-infrared supercontinuum sources for analysis of the species inside methane and carbon dioxide plasmas and the products formed in the outflow.

1. Introduction

Fourier transform spectroscopy in the infrared spectral region (FTIR) is a well-established method for a wide range of applications. Classical FTIRs offer broad spectral coverage with sufficient spectral resolution for multispecies detection in the gas phase. However, these systems are traditionally equipped with incoherent thermal light sources that are omnidirectional and offer a low spectral brightness. Consequently, this restricts the detection sensitivity for the species to be investigated. Currently, novel ultra-broadband mid-infrared supercontinuum (SC) light sources are emerging, as a good candidate to replace the incoherent thermal light sources in FTIRs. Recent demonstrations show SC sources with a spectral coverage of 1.5-10.5 μm [1]. These sources are spatially coherent and outperform thermal sources in spectral brightness. Recently, our group developed a Fourier transform spectrometer, built specifically to make full use of the advantages of the SC source, while also dealing with its Relative Intensity Noise (RIN), a potential downside of a SC source [2]. Here, we present the application of this system for analysis of methane and carbon dioxide in electrical discharge plasmas.

Electrical discharge plasmas, driven by sustainable energy, are emerging as potential candidates to reduce CO_2 emissions in the atmosphere. Inside a plasma of CH_4 and CO_2, several reactions take place, such as dehydrogenation of CH_4 and its conversion to higher hydrocarbons (e.g. ethane, ethylene and acetylene), or the conversion of CH_4 and CO_2 into CO and H_2 (syngas). Studying these plasmas is of great interest to get a detailed understanding of the kinetic processes inside the plasma. Analyzing the outflow of the plasma reactor provides an overview of the total conversion and the products formed. Additionally, the spatial coherency and high brightness of the SC source enable us to analyze the compounds inside the plasma, which is a unique advantage over classical FTIRs. This way, it is possible to observe the temperature-dependent rotational distribution and vibrational excitation of the molecules during the discharge.

2. Experimental setup and results

The CH_4 and CO_2 plasmas were created in a water-cooled, glow-discharge plasma cell (180 cm length with 1.5 cm internal diameter). The plasma cell has an anode and gas inlet in the center and two cathodes and gas outlets at both ends of the tube. One end of the cell has a Brewster window through which the light beam can travel, while the other end has a flat mirror to reflect the light beam. A direct current (DC) electrical discharge is generated in the cell using a current-stabilized high-voltage power supply (25 kV, 40 mA). Two different supercontinuum sources were used with the setup. The beam of a SC source from NKT Photonics (SuperK MIR) with a spectral coverage of 1.4 – 4.1 μm (~450 mW, repetition rate 2.5 MHz) was sent through the discharge cell to analyze the molecular species inside the plasma. The second SC source was developed by DTU Fotonik (spectral coverage 4.0 - 7.5 μm, power ~86 mW, repetition frequency 3.0 MHz). Its beam is directed through a Herriot multipass cell (nominal optical path length 31.2 m) located in the outflow of the gas from the discharge tube.

After passing through the plasma cell or the multipass cell, each of the SC beams is sent to a separate, home-built Fourier transform spectrometer (FTS, spectral resolution 1 GHz). The setup of the FTS has been described elsewhere [2]. In short, the incoming beam is split into two arms, both leading to a corner cube retroreflector mirror. In contrast to a classical interferometer, both retroreflector mirrors are mounted to a linear stage, thereby doubling the maximal optical path difference. The retroreflector mirrors impose a slight lateral shift in the beam path upon reflection, so that the superposition of the two beams after recombination on the beamsplitter can propagate towards two separate MCT photovoltaic detectors. The two interferograms recorded by the detectors are out of phase with in-phase noise. Consequently, the two signals are subtracted in a balanced detection scheme to improve the signal-to-noise ratio. A Fast Fourier transform (FFT) is performed to calculate the spectrum of the interferogram. A He-Ne laser beam is sent through the same FTS setup to calibrate this spectrum in the wavenumber domain. In addition, the beam path of the

long wavelength SC source (DTU Fotonik) is purged with N_2 gas to minimize the H_2O and CO_2 absorption outside of the multipass cell in the recorded spectrum.

To enable proper analysis of the absorbance spectra of the species inside the plasma, it is necessary to consider the total internal partition function in the HITRAN parameters for the simulation. Figure 1 (a) shows the measured spectrum of CH_4 (in black, the R-branch) during the discharge, alongside the fitted model spectrum of CH_4 considering the ground state transition to the ν_3 vibrational band and the corresponding partition function for the line intensity distribution of the rotational lines (in red, inverted), as well as a fitted model for hot bands (transitions in the vibrational exited states) of CH_4 (in blue, inverted). We achieve an excellent agreement between the measurement and simulations, considering a temperature of 567 K for the rotational distribution of CH_4 molecules inside the plasma and a temperature of 682 K for the vibrational excitation (which becomes apparent as hot bands). The discrepancy of the two retrieved temperatures can be explained by the more effective cooling of the rotational energy inside the plasma. Figure 1 (b) shows the absorbance spectra of the reaction products in the outflow of a plasma of 70/30% CH_4/CO_2. The broad spectral coverage enables simultaneous detection of many different reaction products, while the high spectral resolution of 3 GHz allows for unambiguous identification, even for species with overlapping absorption features. Analysis of the outflow of reaction products is used to determine the final concentration of the species formed inside the plasma, which for this specific reaction turned out to be 32±2% CO, 14±1% CO_2, 0.73±0.03% ethylene, 0.13±0.01% formaldehyde, 0.3±0.1% acetone and 0.3±0.1% acetaldehyde.

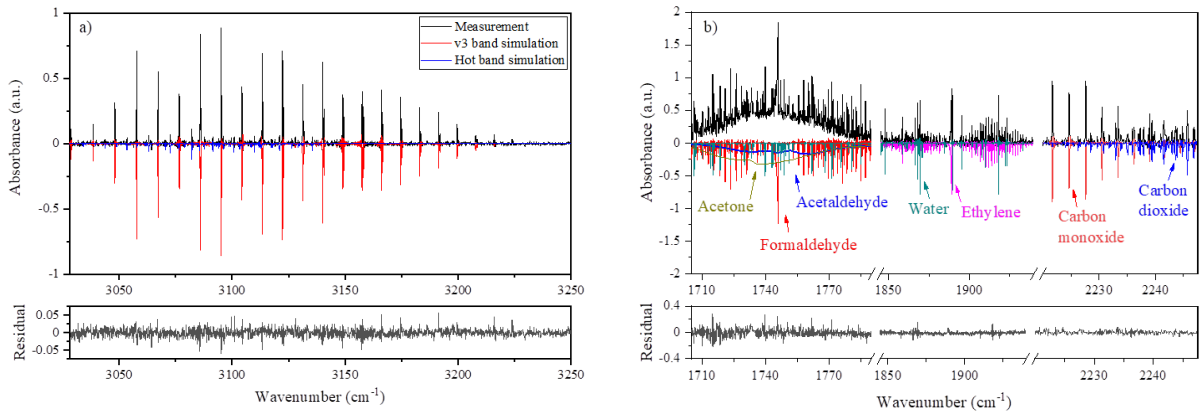

Fig.1: (a) Measured spectrum of the observed R-branch of the ν_3 band of methane during discharge (in black). The best fit of the simulations for the ν_3 band and hot bands of methane are found for rotational and vibrational temperatures of 567 K and 682 K, respectively (inverted, in red and blue). (b) Measured spectrum of the reaction products of a 70% CH_4 with 30% CO_2 discharge (specific energy input: 11 MJ/mol, in black). Reference spectra of formaldehyde, water, carbon monoxide, carbon dioxide (from HITRAN), acetone and acetaldehyde (from PNNL) and ethylene (from GEISA) shown inverted.

3. References

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