Mid-infrared dual-comb spectroscopy for high-speed chemical kinetics measurements in a shock tube

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Abstract: We report high-speed measurements of chemical kinetics reactions inside a shock tube using a 1-GHz repetition rate mid-infrared dual-comb spectrometer. We show formation of formaldehyde and sub-sequent decomposition to carbon-monoxide with 17.5 µs time resolution.

Dual-frequency comb spectrometers (DCS) based on fiber mode-locked lasers are broadband, high-resolution spectrometers capable of multi-species detection. The majority of DCS demonstrations have been with 100-200 MHz repetition rate frequency combs and required averaging times of seconds to minutes to achieve high signal-to-noise ratio (SNR). The averaging requirement stems from low power per comb mode of 100-200 MHz combs resulting in low single-shot SNR. Increasing the repetition rate of the frequency comb results in higher power per mode, hence higher single-shot SNR, and an overall improvement of the DCS time resolution [1]. The SNR can be further improved by operating in the mid-infrared (MIR) spectral region to access the strong fundamental absorption transitions of molecules. Here, we demonstrate a high-speed MIR DCS with 1 GHz repetition rate and comb tooth spacing. We use this spectrometer to study the chemical kinetics of 1,3,5-Trioxane in a shock tube with 17.5 µs time resolution.

Our DCS is based on MIR frequency combs generated through the intra-pulse difference frequency generation (IP-DFG) process inside a $\chi^{(2)}$ nonlinear crystal. The driving pulse for the IP-DFG process is an 8 fs (sub-two-cycle) pulse at 1.56 µm with ~ 2 W of average power at 1 GHz repetition rate [2][3]. The $\chi^{(2)}$ nonlinear crystal used here is a fan-out periodically poled lithium niobate (PPLN), which generates an offset-free frequency comb covering the entire 3-5 µm region simultaneously with no gap in the spectrum. The average optical power from each comb is ~4 mW. Figure 1 shows the schematic of the mid-infrared DCS setup with light from both combs combined in free space and then coupled into InF_3 fiber [4].

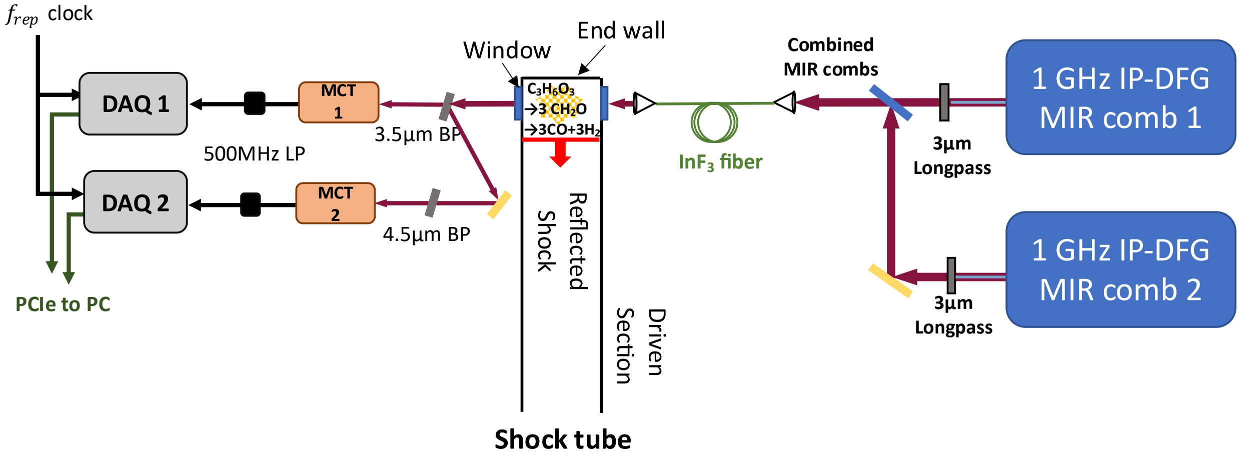

Fig. 1. Chemical kinetics study in a shock tube using 1 GHz MIR DCS. The light from the two 1-GHz MIR frequency combs are combined in free space and coupled into an InF_3 fiber and sent to the shock tube. After passing through the shock tube (12.7 mm optical path) the light is spectrally filtered and sent to two separate MCT detectors for parallel and simultaneous detection of CO and H2CO.

MIR light is sent to the shock tube experiment over fiber, where it is collimated and sent through an optical access close to the end wall of the shock tube. The shock tube is a miniature high repetition rate shock tube [5] with a 12.7mm inner diameter that sets the optical interaction path length. After passing through the shock tube, the light is spectrally separated using two optical bandpass filters centered at 3.5 and 4.5 μm as shown in Fig. 1. The light transmitted through the first filter (3-4 μm) is sent to a fast mid-infrared MCT detector. The light reflected from this filter is then filtered again to transmit the 4-5 μm region to a second MCT detector. This filtering and parallel detection scheme allows for higher single-shot SNR and hence better overall time resolution. The spectral regions and the number of filters are chosen based on the target molecules. The heterodyne beats are lowpass filtered and digitized using two 1 GS/s data acquisition cards.

We studied the formation of formaldehyde (H_2CO) from the decomposition of 1,3,5-Trioxane ($C_3H_6O_3$), and its subsequent decomposition to carbon monoxide (CO). The broad bandwidth and the high-speed capability of our spectrometer allows for simultaneous detection of CO and H_2CO. For these experiments, interferograms and the resulting absorbance spectra are measured at 56 kHz rate and averaged over 800 repeat firings of the shock tube. Fig. 2(a) shows the time resolved concentration of H_2CO and CO with 17.5 μs time resolution. We can clearly see the formation of H_2CO and its subsequent decomposition to CO after the reflected shock. In addition to the concentration, we are able to extract the gas temperature inside the shock tube using >30 well-resolved CO absorption features, with greater accuracy than has been demonstrated before. Fig. 2(b) shows the time-resolved temperature inside the shock tube, showing the increase of the temperature from ~300K to as high as ~1600K after the reflected shock.

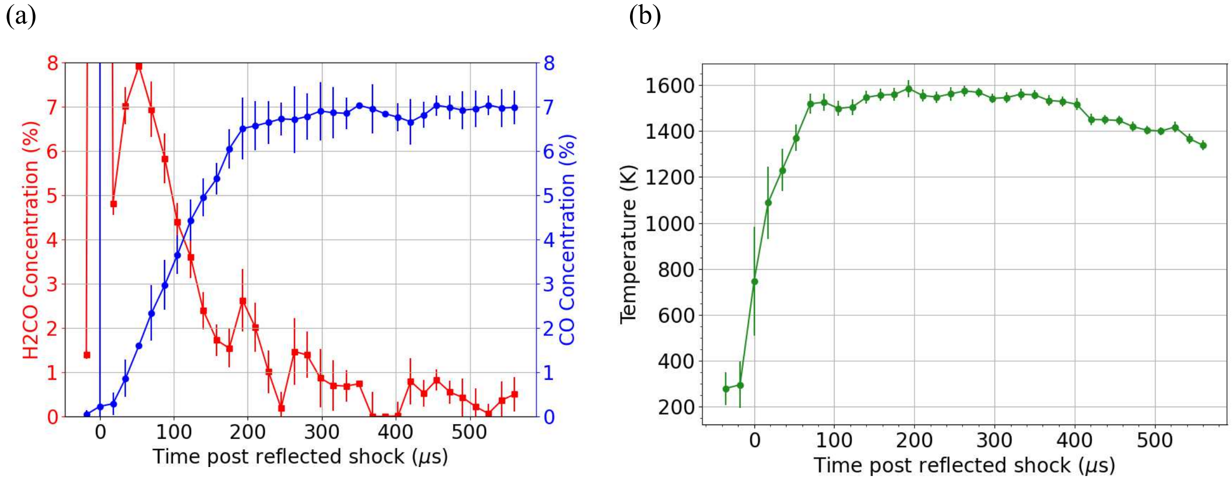

Fig. 2. (a) Time resolved concentration of H2CO and CO after reflected shock. The formation of H2CO and its subsequent decomposition to CO is clearly evident with the 17.5 μs time resolution. (b) Accurate measurement of temperature of the gas inside the shock tube using our spectrometer. This is the first simultaneous measurement of the H_2CO and CO concentrations together with temperature with laser absorption spectroscopy.

The accurate knowledge of temperature and concentration are critical for understanding the chemical kinetics in shock tube experiments. These results show that broadband, 1 GHz repetition rate mid-infrared dual-comb spectrometers are now available as a powerful tool for studying the fundamentals of chemical kinetics.

References

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