Chemical kinetics study with a GHz mid-infrared dual-comb spectrometer

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Abstract: We study abundance and temperature of species in reactant to product breakdown of 1,3,5-trioxane inside a shock-tube using a 1 GHz repetition rate mid-infrared dual-comb spectrometer with optical bandwidth > 30 THz. © 2024 The Author(s)

In situ diagnostics of chemical kinetic using laser spectroscopy techniques can help understand the reaction pathways and rates. The ideal laser diagnostics tool should provide information on the abundance of the all the species involved in the reaction, from reactant to product with high accuracy and specifity at relevant time scales. It should also provide accurate temperature measurement simultaneously. Here we demonstrate the first laser absorption spectrometer that can achieve all these metrics for chemical kinetics studies.

Our spectrometer is a mid-infrared dual-comb spectrometer with 1 GHz repetition rate and broad bandwidth of >30 THz in C-H stretch region. The spectrometer can have <20 μs acquisition time while maintaining a broad acquisition optical bandwidth and high spectral resolution of 1 GHz (0.03 cm^{-1}).

To achieve broad optical bandwidth mid-infrared frequency combs, we start with commercially available 1 GHz near-infrared mode-locked lasers with center wavelength at 1560 nm. We amplify the pulses to ~4 W average power using an all-in-fiber chirped pulsed amplification scheme. We then compress the pulses in a grating compressor and generate a sub-two cycle pulses using soliton self-compression in anomalous dispersion highly nonlinear fiber (HNLF). We generate broadband mid-infrared frequency combs based on robust and single pass intra-pulse difference frequency generation (IP-DFG) technique in a $\chi^{(2)}$ nonlinear crystal. Using a fan-out periodically poled lithium niobate crystal (PPLN), we obtain mid-infrared spectrum that spans the entire 3-5 μm region (> 30 THz) with no gap [1].

The two degrees of freedom of the NIR comb is stabilized. This is done by stabilizing a beat note between a comb line in NIR and a narrow linewidth laser and the career envelope offset beat (f_{ceo}). f_{ceo} is obtained from the cascaded $\chi^{(2)}$ processes inside the PPLN crystal used for IP-DFG.

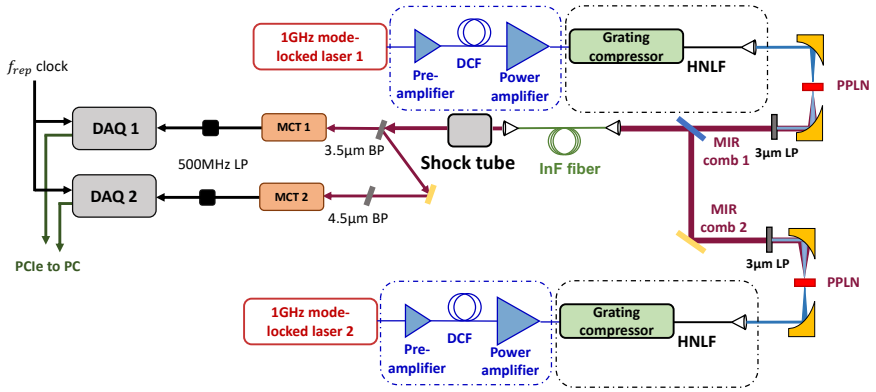

Fig. 1. High-speed mid-infrared dual-comb spectrometer setup. The light from the two 1-GHz MIR frequency combs is combined in free space and coupled into an InF_3 fiber and sent to the shock tube. After passing through the shock tube (12.7 mm optical path) the light is spectrally filtered and sent to two separate MCT detectors for parallel and simultaneous detection of CO and H_2CO.

We built the dual-comb spectrometer with two mid-infrared frequency combs with very similar characteristics in terms of the generated optical power and bandwidth. Acquisition rate of the dual-comb spectrometer which is defined by the difference in repetition rate of the two combs, can be tuned from few Hz to 100kHz [2].

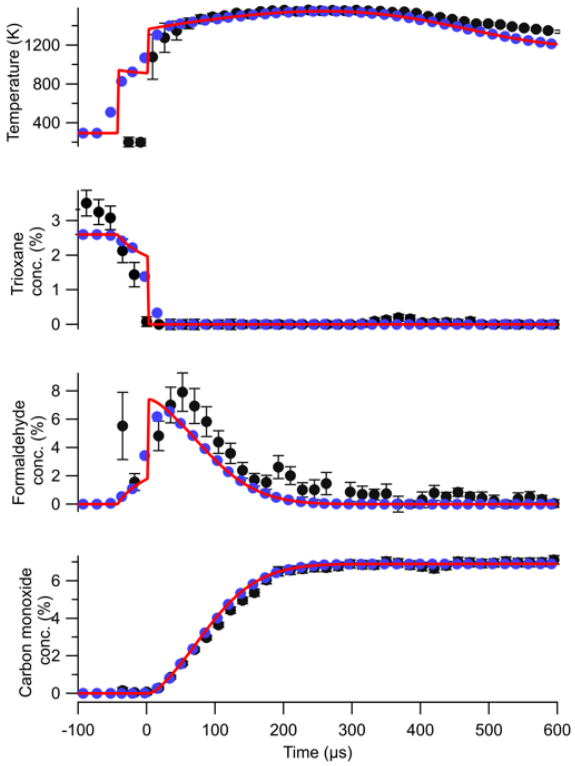

Figure 2. Time resolved mole fraction and temperature with 17.5 μs time resolution measured with GHz mid-infrared DCS (black markers) and comparison with simulations (blue markers and red lines) for experiments with 2.6% $C_3H_6O_3$ in argon.

Using this spectrometer, we studied formation of formaldehyde (H_2CO) from the decomposition of 1,3,5-Trioxane, and its sub-sequent decomposition to carbon monoxide (CO). Since the spectrometer has bandwidth > 30 THz, we can simultaneously detect CO and H_2CO which absorb at 4.5 μm and 3.5μm regions respectively. The absorbance spectra are measured at 56 kHz rate (17.5 μs) and averaged over 800 repeat firings of the shock tube. We are also able to measure the gas temperature with high accuracy from the measured CO absorbance spectra. Fig. 2 shows the time resolved mole fraction of $C_3H_6O_3$, H_2CO and CO measured by our spectrometer (black dots) and simulation results (red line). In addition, the optically measured gas temperature and simulation with 17.5 μs time resolution are shown as well.

In summary, we developed a 1 GHz repetition rate mid-infrared dual-comb spectrometer based on IP-DFG and demonstrated its application in chemical kinetics studies inside a shock tube.

References

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2. P. Chang, N. Hoghooghi, S. Egbert, S. Xing, D. Lesko, A. Lind, G. Rieker, S. Diddams, “1 GHz mid-infrared dual-comb spectrometer spanning more than 30 THz” in *Conference on Lasers and Electro-Optics* (Optica Publishing Group, Washington, D.C., 2022), p. SF4O.4.